

SEMIEMPIRICAL CALCULATIONS OF GROUND STATE PROPERTIES AND ROTATIONAL BARRIERS IN CONJUGATED ETHYLENES

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Abstract—Ground state properties of methyl-2-carbomethoxy-3-dimethylaminoacrylate **4**, and methyl-2-carbomethoxy-3-(1-aziridino)acrylate **5** were calculated by semiempirical methods and found to be in good agreement with the experiment. Barriers to rotation about the C=C double bond and the C-N single bond were also calculated, allowing for structure relaxation in the transition state. A comparison of the calculated and experimental barriers to rotation shows good agreement for the rotation about the C-N bond and poor agreement for the rotation about the C=C bond. This discrepancy is explained in terms of solvent stabilization of the polar transition state.

The barriers to rotation about formal single and double bonds in different types of molecules were investigated very thoroughly by various spectroscopic techniques. In molecules of type 1, two rotational processes are of interest, namely, the rotation about the C=C double bond and the rotation about the C-N single bond. With the appropriate structural substitution of the double bond (R_1 and R_2 are electron withdrawing groups) and the C-N bond, processes may be studied by NMR techniques.¹⁻³ In this work we have investigated these processes by semiempirical quantum chemical calculations on the two model-molecules **2** and **3**, shown in Fig. 1. All the calculations were performed by the INDO method.^{4,5} Sandstrom *et al.* have carried out LCAO-MO calculations of the ground state of similarly polarized olefins.⁶

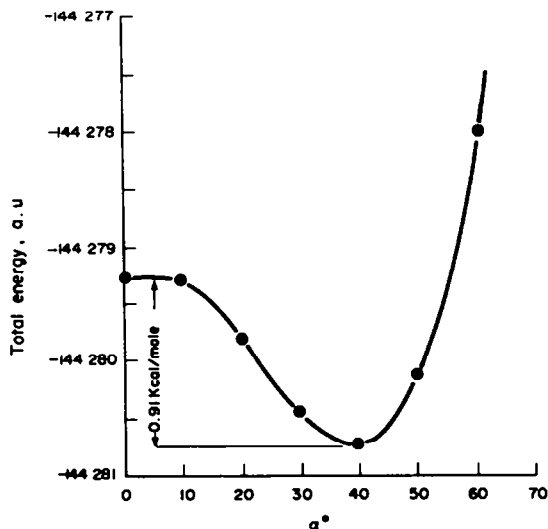
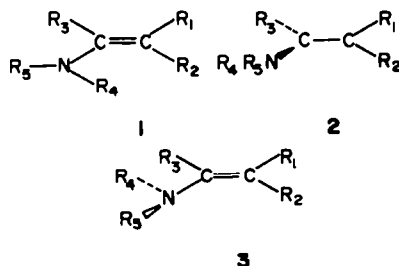


Fig. 1. INDO total energy of **5** vs. α , the out-of-plane distortion angle of the aziridino group.

double bond plane. The X-ray crystallographic structure is schematically depicted in Fig. 1(4).

Naturally, determination of the ground state structure of **4** would involve the optimization of all bond lengths and bond angles. However, considering the size of the molecule and consequently the large number of structural parameters this would be an enormous task. We believe that the selection of specific and important structural parameters may provide a reasonable understanding of the features that affect the structure of the molecule. The following structural parameters were selected: the C=C and C-N bond lengths, the conformation of the carbomethoxy group (A) and the configuration of the dimethylamino N atom. By varying the bond lengths while keeping all other parameters constant, and assuming that the potential energy behaves like a second-order polynomial, it was possible to establish the minimum energy bond lengths. The conformational energies involved in the rotation of the carbomethoxy group (A) were calculated for the dihedral angles 67° and 0° (the latter implies an all-planar struc-

1. **Ground state properties.** The quality of calculated ground state properties is subject to the quantitative agreement with the experimental results. The structure of **4** was determined by X-ray crystallography⁷ and may be characterized by the following important features: (a) the C=C bond (1.380 Å) is longer and the C-N bond (1.337 Å) is shorter than in the respective non-conjugated analogs, (b) the dimethyl amino group was found to be co-planar with the C(9)-C(10)-C(1)-O(2) part of the molecule, and (c) the carbomethoxy group *cis* to the dimethylamino moiety, (A), is rotated by 67° out-of-the

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Table 1. Calculated and experimental structural parameters of 4 and 5

Structural Parameter [§]	4		5
	INDO (calc.)	Exp. [†]	INDO (calc.)
C(9)–C(10) bond length (Å)	1.37	1.380 ± 0.0005	1.36
C(9)–N(11) bond length (Å)	1.32	1.337 ± 0.0004	1.37
Conformation of CO ₂ CH ₃ (A)	twisted (67°) [‡]	twisted (67°)	co-planar
Configuration of N(11)	planar	planar	non-planar [¶]

[†]See Ref. 6. [‡]The all-planar structure is 2.35 kcal/mole higher than the twisted one. [§]For the numbering of the atoms see Fig. 1. [¶]The out-of-plane angle (α) is 40° and the energy of the planar structure is higher by 0.91 kcal/mole.

ture). The configuration of the dimethylamino N atom was studied by calculating the energies of the two extreme structures namely the planar and the pyramidal systems. Table 1 summarizes the INDO and the experimental results and it is clear that there is very good agreement between the calculated and the experimental structural parameters of 4.

Before discussing the calculated structural parameters of 5 we would like to point out a few facts. Firstly, there is no experimentally determined structure for 5 but, since 4 and 5 are structurally similar, it is reasonable to assume that the same factors are responsible for the structure of both molecules. Secondly, the good accord between the calculated and experimental structures of 4 makes the calculated structure of 5 quite probable. Thirdly, the coordinates of the aziridino group were taken from microwave study.⁸

The calculated structural parameters of 5 are presented in Table 1. In establishing the structure of 5 the configuration of the aziridino N atom is an important issue since it affects all the other structural parameters. Figure 2 shows the INDO total energy as a function of the out-of-plane angle of distortion (α) of the aziridino ring with respect to the plane determined by N(11), C(9) and C(10). It is clearly evident that the most stable geometry of the aziridino group is a non-planar one⁹ with an angle of distortion (α) of 40°, resulting in an inversional barrier of 0.91 kcal/mole. The consequences of the pyramidalization of the aziridino group become apparent when other structural parameters are analyzed. Thus, the CO₂CH₃(A) group in 5 no longer suffers from steric interaction present in 4 and therefore prefers the co-planar conformation. Moreover, the C(9)–N(11) bond becomes longer due to a better localization of electrons, and consequently the C(9)–C(10) bond becomes shorter than in 4.

2. Charge population and bond orders. It is of interest to compare the charges on various atoms in 4 and 5 as they serve to clarify the differences, as well as the similarities between the two molecules. In Table 2 net and π -charges of some selected atoms of 4 and 5 are presented. One immediately notices the alternating charges on the atomic skeleton N(11)–C(9)–C(10)–C(1)–O(2) in both molecules. Bearing in mind the strongly electronegative character of the O atom this kind of polarization is readily understood. However, the negative charge on the N atom is surprising when it is recalled that the N electrons are delocalized on the C(9)–C(10)–C(1)–O(2) structure. The net charge on an atom can be considered as the sum of π - and σ -charges, the former being the charge in the orbital perpendicular to the plane of the molecule. Indeed the positive π charge on the N atom (Table 2) reflects the extensive delocalization of the p electrons. But, here lies the main difference between the N and the rest of the atoms. While the net and π -charges on the carbons and the oxygen have the same sign, indicating the same type of polarization in the π - and the σ -sub-systems, the net and π -charges on the N

Table 2. Net and π -charges of various atoms in 4 and 5

Atom	Net Charges		π -Charges [†]	
	4	5	4	5
N(11)	–0.115	–0.140	+0.290	—
C(9)	+0.254	+0.269	+0.142	+0.167
C(10)	–0.282	–0.253	–0.251	–0.196
C(1)	+0.537	+0.526	+0.214	+0.211
O(2)	–0.434	–0.424	–0.434	–0.417

[†] π -Charge is the charge in the orbital perpendicular to the plane determined by the listed atoms.

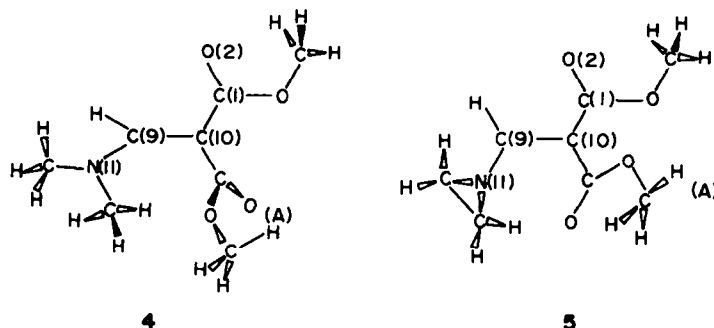


Fig. 2. Spatial arrangement and numbering of the atoms in the ground states of 4 and 5.

have opposite signs. This must be the result of two opposite effects namely, the donation of charge through the π -system and the withdrawal of charge through the σ -system. Both effects, although acting in opposite directions, mutually enhance each other. In other words, as more charge is donated through the π system, the N becomes more electronegative, thus withdrawing more σ -charge. This phenomenon, i.e. the "softness" of the sub-systems of the N atom, is in our opinion responsible for the small negative net charge and will probably cause an insensitivity of the charge to the degree of delocalization.

Table 2 also shows the main difference between 4 and 5. The two molecules are strictly not comparable in the N(11)-C(9) region due to structural differences (4 has a planar N whereas 5 has a pyramidal one), but the smaller extent of polarization in 5 is reflected by the magnitude of the charges on C(10), C(1) and O(2). The differences between the π -bond-orders among various atoms of 4 and 5 (Table 3), also substantiate the differential polarization of the above two molecules.

Table 3. π -Bond orders between various atoms

Bond	π -Bond-Order	
	4	5
N(11)-C(9)	0.505	(0.429) [†]
C(9)-C(10)	0.787	0.802
C(10)-C(1)	0.358	0.327
C(1)-O(2)	0.802	0.794

π -Bond order in 5 with a co-planer aziridino group.

The dipole-moment of 4 and 5 is a physical property closely related to the distribution of electronic charges in the molecule. The calculated values for 4 and 5, are 4.30 D and 1.94 D respectively, and the moments are pointing in the general direction from the N to the C(1)-O(2) bond and forming an angle of 41° with the C(9)-C(10) bond. Once again, the substantial difference in the dipole-moments indicates that the polarization in 5 is smaller than in 4.

3. *Structure of the transition states to rotation about C(9)-C(10)*. The most important structural change which takes place during the rotation about the C(9)-C(10) bond is in the torsional angle N(11)-C(9)-C(10)-C(1), which changes from 0° to 90°. It is very reasonable to assume that the 90° conformation (3) represents the geometry of the transition state, as in this geometry the p_z 's on C(9) and C(10) do not overlap. The question is what other structural parameters undergo relaxation in this transition state. In 4 we have chosen to vary the C(9)-C(10)

and N(11)-C(9) bond lengths as well as the conformation of the carbomethoxy group. In 5 the change in the conformation of the carbomethoxy group was, of course, unimportant (being planar in the ground state), and instead, the configuration of the aziridino group was varied.

The structural change in the transition states of the rotation about C(9)-C(10) are summarized in Table 4. It is evident (Table 4) that the C(9)-C(10) bond length in both 4 and 5 increases in the transition state when compared to the respective value in the ground state (Table 1). The result is compatible with the simple idea of "breaking" the π bond in the transition state. The behavior of the C(9)-N(11) bond is different. In 4 there is no change in this bond length but in 5 a contraction of the bond occurs. This behavior is directly related to the configuration of N(11) in the transition state. From the data of Tables 1 and 4 it follows that during the rotation about C(9)-C(10) the configuration of N(11) does not change in 4 (remains planar) whereas it does change from pyramidal to planar in 5, resulting in a better overlap between the N(11) and C(9) p orbitals and consequently in the shortening of the N(11)-C(9) bond. Another structural change which takes place in 4, but obviously cannot occur in 5, is in the conformation of the CO₂CH₃(A) group. The co-planarization of this group in the transition state of 4 is a consequence of the vanishing of the steric interaction which is present in the ground state. As a result of this conformational change the energy of the transition state of 4 is lowered by 13.1 kcal/mole. Naturally, as there is no such change in the conformation of the CO₂CH₃(A) group in 5, the process is affected to the extent that the ground state is free of non-bonded interactions.

4. *Charge population in the transition state to rotation about C(9)-C(10)*. Inspection of the charge population in the transition state to rotation about C(9)-C(10) provides better understanding of the rotational process. The charges are summarized in Table 5.

When comparing Tables 2 and 5 it can be seen that the major change is in the charges on C(9) and C(10). There is a remarkable polarization of the bond with the charge

Table 5. Net and π -charges in the transition state to rotation about C(9)-C(10)

Atom	Net charge		π -Charge	
	4	5	4	5
N(11)	-0.038	+0.040	+0.494	+0.492
C(9)	+0.398	+0.399	+0.350	+0.348
C(10)	-0.451	-0.455	-0.527	-0.532
C(1)	+0.564	+0.571	+0.217	+0.219
O(2)	-0.498	-0.465	-0.511	-0.480

Table 4. Structural and energy parameters of the transition states to rotation about C(9)-C(10)

Structural parameter	4	5
C(9)-C(10) bond length (Å)	1.42	1.39
N(11)-C(9) bond length (Å)	1.32	1.35
Conformation of CO ₂ CH ₃ (A)	Co-planar	Co-planar
Configuration of N(11)	Planar	Planar
E _{TS} -E _{GS} (calc.) (kcal/mole) [†]	34.8	54.1
$\Delta H^\ddagger_{(298^\circ K)}$ (exp.) (kcal/mole)	8.3	> 25.5

[†]E_{TS} and E_{GS} are the calculated transition and ground state energies.

shifting from C(9) to C(10), thus respectively increasing both the positive and negative charges on these atoms. Other atoms are also affected by this polarization as may be seen from the increase in the positive π -charge on N(11) and the negative charge (net and π) on O(2). This is the result of the delocalization of the negative charge on C(10) onto the malonate moiety and the nitrogen lone pair into the partially vacant orbital on C(9). We believe that this delocalization is very important in stabilizing the transition state for rotation about the C(9)–C(10) bond.

The "softness" of the electronic charge of the N atom may also be observed here. The increase in the positive π -charge due to electron transfer from the N lone pair into the vacant orbital on C(9) has increased the electro-negativity of the N atom resulting in a larger withdrawal of σ -charge. Consequently, the net charge on the N atom of 4 has changed by only 0.077 e.u. whereas the other charges changed by more than twice this amount.

There is a striking similarity between the structures and the properties of the transition states of 4 and 5. For example, in both molecules the $\text{CO}_2\text{CH}_3(\text{A})$ group is in a co-planar conformation and the N is in a planar configuration (Table 4). The charge distribution (Table 5) and consequently the dipole-moments are also similar: 6.03 D and 5.55 D for 4 and 5, respectively. This suggests that the polarization in the transition states of 4 and 5, resulting from the heterolytic fission of the double bond, imposes structural changes in order to provide maximal stabilization of these states. Thus, the $\text{CO}_2\text{CH}_3(\text{A})$ group in 4 rotates into a co-planar conformation in order to delocalize the negative charge on C(10), and the aziridino group in 5 acquires a planar conformation to delocalize its N lone-pair into the vacant orbital on C(9). The similarity, therefore, reveals the general nature of the transition states to rotation about the C(9)–C(10) bond in 4 and 5, and most probably in structurally similar systems.

5. *The barriers to rotation about C(9)–C(10).* We may now proceed to analyse the calculated and experimental barriers to rotation about C(9)–C(10). The experimental barrier (ΔH_{298}^\ddagger) for 4, as was measured by DNMR technique,¹⁰ is 8.3 kcal/mole. Unfortunately, the NMR spectrum of 5 did not show any changes up to 200° and therefore only a lowest limit of the barrier could be estimated as 25.5 kcal/mole. The calculated barrier values for 4 and 5, obtained by subtracting the energy of the ground state from that of the transition state, are 34.8 and 54.1 kcal/mole respectively (Table 4).

The large discrepancy between the calculated and measured barriers may be attributed to the different conditions under which the calculations and the measurements were performed. The calculated values are related to *vacuo* and at 0°K, whereas the measurements were performed in solutions (4; 0.1M, in CH_2Cl_2

and 5; 0.1M in C_4Cl_6), and over a range of temperatures. Although the temperature effect was practically eliminated by employing a total NMR lineshape analysis, the stabilizing energy of the solvent could not be estimated, and in fact must be taken into account. Considering the large dipole moment of the transition state and the large negative entropy of activation, $\Delta S^\ddagger = -25$ e.u., we believe that solvent stabilization is the main reason for the observed discrepancy. That such solvent effect is indeed operative can be judged from our recent work on similar systems.¹¹ Extrapolation of experimental ΔH^\ddagger values (Table 2 Ref. 11) using Z values of acetonitrile and a hydrocarbon led to a difference of ca 11 kcal/mole. Furthermore, dilution experiments (unpublished results) indicate the importance of solute–solute interaction in lowering the isomerization barrier. Also, the fact that total optimization of all bond angles and bond distances was not performed may contribute to the observed discrepancy.

It is, however, interesting to compare the calculated barriers for 4 and 5 as they are more meaningful and may point to the reason for the difference in the barriers. The barrier may be related to the enhanced charge separation generated in the heterolytic fission of the C(9)–C(10) π -bond. Compounds 4 and 5 reach a similar structure and charge distribution in the transition state, starting from different ground states. But, while in 4 an appreciable stabilization occurs due to the change in the conformation of the $\text{CO}_2\text{CH}_3(\text{A})$ group, there is no comparable effect in 5. Moreover, compound 5, being less polar than 4 in the ground state, requires more energy to generate a similar polarization as 4, which starts from a more polarized ground state.

The difference between the calculated barriers of 5 and 4 is 19.3 kcal/mole, while the experimentally measured barriers are greater than 25.5 and 8.3 kcal/mole respectively. By adding the above calculated energy difference to the measured barrier of 4 we obtain a minimal value of ca. 28 kcal/mole for 5, which is indeed out of the measurable range of NMR technique and in accord with our experimental results. Obviously, this is only an estimated value.

6. *Structure of the transition state to rotation about N(11)–C(9).* As in the previous rotational process the transition state was assumed to possess a geometry where the rotational angle about the N(11)–C(9) bond is 90° as depicted in 3. It is on this structure that optimizations of the N(11)–C(9) and C(9)–C(10) bond lengths and the configuration of the nitrogen atom were performed. In 4 the conformation of the $\text{CO}_2\text{CH}_3(\text{A})$ group was varied in order to obtain the lowest energy. The structural parameters of the transition states to rotation about N(11)–C(9) for 4 and 5 are summarized in Table 6.

Here also, as in the previous rotational process,

Table 6. Structural and energy parameters of the transition state to rotation about N(11)–C(9)

Structural parameter	4	5
C(9)–C(10) bond length (Å)	1.35	1.35
N(11)–C(9) bond length (Å)	1.37	1.39
Conformation of $\text{CO}_2\text{CH}_3(\text{A})$	Co-planar	Co-planar
Configuration of N(11)	Pyramidal	Pyramidal
$E_{\text{TS}} - E_{\text{GS}}$ (calc.) (kcal/mole)†	8.9	5.1
ΔH_{298}^\ddagger (exp.) (kcal/mole)	12.9	< 7.0

† E_{TS} and E_{GS} are the calculated transition and ground state energies.

changes in bond lengths do occur, but this time the N(11)–C(9) bond lengthens and the C(9)–C(10) bond shortens in both molecules. Indeed, these phenomena are compatible with the vanishing of p - π interaction in the orthogonal transition state. Again, with the disappearance of the steric interaction present in the ground state of **4**, the $\text{CO}_2\text{CH}_3(\text{A})$ group in the above transition state adopts co-planar conformation; the stabilization due to this process amounts to 1.4 kcal/mole only. This value is a good measure of the non-bonded interaction between the *cis* Me_2N and CO_2CH_3 groups. The N atoms in the transition states of both **4** and **5** were found to be pyramidal.

7. *Charge population in the transition state to rotation about N(11)–C(9)*. The charges on selected atoms in the transition state to rotation about N(11)–C(9) are given in Table 7. It is immediately apparent that the transition state to this process is characterized by a smaller polarization than the ground state. This may be attributed to the localization of electrons on the N atom, as may be seen from its larger negative charge. Once the delocalization of the N lone pair has been excluded by the 90° rotation of the amino group, there is no longer any reason for the N to remain in a planar configuration. Therefore the N atom in **4** undergoes a pyramidalization during the rotation about N(11)–C(9), which stabilizes the transition state by 3.4 kcal/mole. Finally, the smaller polarization of this transition state is also reflected by the dipole moments which are 0.86 D and 1.92 D for **4** and **5** respectively.

Table 7. Net and π -charges in the transition state to rotation about N(11)–C(9)

Atom	Net charge		π -Charge	
	4	5	4	5
N(11)	–0.197	–0.165	—	—
C(9)	+0.280	+0.276	+0.184	+0.180
C(10)	–0.223	–0.230	–0.134	–0.158
C(1)	+0.522	+0.523	+0.209	+0.210
O(2)	–0.409	–0.416	–0.400	–0.407

8. *The barriers to rotation about N(11)–C(9)*. The enthalpy of activation (ΔH^\ddagger_{298}) for the rotation about N(11)–C(9) in **4**, as was measured by NMR technique, is 12.9 kcal/mole.¹⁰ In the case of **5** even lowering of the temperature down to -120° did not result in measurable changes in the NMR lineshape, therefore only the upper limit to the barrier of the above rotational process could be estimated as being 7 kcal/mole.¹⁰ The calculated barriers for **4** and **5** (Table 6) are in agreement with the experimental results as far as their trend is concerned. Also, the calculated barrier for this process in **5** (5.1 kcal/mole) is well below the measurable limits of DNMR, in agreement with the experimental results. The value for the calculated barrier in **4** is, however, smaller than the experimental one. Obviously, the argument of not optimizing the whole structure does not apply here; however we again note the solvent effect. Considering that the transition state to this rotational process is less polar than the ground state, solvent stabilization is more effective in the ground state and is reflected by the positive entropy of activation ($\Delta S^\ddagger = +2$ e.u.) as measured by NMR technique.¹⁰ Thus, the INDO cal-

culations when not taking into account the effect of the solvent, underestimate the barrier to rotation about the N(11)–C(9) bond. This underestimation will be enhanced in the case of **4** as compared to **5** due to the larger change in the polarity during the rotational process in **4**.

CONCLUSION

There is a great deal of similarity in the behavior of the two molecules which were examined here, but, naturally, the differences are of greater interest. The differential capacity of delocalization of the lone pair on the N atom in **4** and **5** is responsible for the differences in the ground state structures of these molecules. On the other hand, the severe electronic requirements in the transition state to rotation about C(9)–C(10) produce a structurally similar transition state in **4** and **5**, and consequently make the barriers very different. When the rotation about N(11)–C(9) is considered, it is seen that the structure of the transition states of **4** and **5** is also similar, but this time there is little difference in the barriers. This is due to the following behavior. During the rotation about N(11)–C(9) of **4** the π -overlap between the lone pair and the rest of the molecule is destroyed. Consequently, the N atom now prefers its more stable pyramidal configuration, thus stabilizing the transition state. The π overlap in **5** is much smaller to start with due to the pyramidal configuration of the N atom in the ground state. Therefore, less energy is required to destroy any existing p - π overlap, and also there is no stabilization due to pyramidalization in the transition state.

We believe that the merits of the present calculations lie not only in the particular molecules and processes which were analyzed, but much more important in revealing the particular structural parameters which are decisive in determining the structure and relative energy of the ground and various thermal transition states. Thus, the N configuration and the conformation of the $\text{CO}_2\text{CH}_3(\text{A})$ group were found to be interrelated and most crucial in determining the energy of the ground and transition states for the two rotational processes. The calculated charge distribution and dipole moments are most instructive considering that the thermal rotational processes are observed and studied in solutions. Furthermore, the above general information and conclusions may now be applied to the analysis of similar systems and processes.

REFERENCES

- Y. Shvo and H. Shanan-Atidi, *J. Am. Chem. Soc.* **91**, 6683, 6689 (1969).
- Y. Shvo, *Tetrahedron Letters* 5923 (1968).
- Y. Shvo, E. C. Taylor and J. Bartulin, *Ibid.* 3259 (1967).
- J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.* **47**, 2026 (1967).
- J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York (1970).
- J. Sandstrom and I. Webberbeck, *Acta Chem. Scand.* **24**, 1191 (1970); E. Ericsson, T. Marnung, J. Sandstrom and I. Webberbeck, *J. Mol. Structure* **24**, 373 (1975).
- U. Shmueli, H. Shanan-Atidi, H. Horwitz and Y. Shvo, *J. Chem. Soc. Perkin Trans II*, 657 (1973).
- B. Baak and S. Skaansys, *J. Mol. Spect.* **10**, 385 (1971).
- F. A. L. Anet and J. M. Osyany, *J. Am. Chem. Soc.* **89**, 352 (1967).
- R. Osman, Ph.D. Thesis, Tel-Aviv University, (1974).
- I. Belsky, H. Dodiuk and Y. Shvo, *J. Org. Chem.* **42**, 2734 (1977).