

THE REACTIVE EXCITED STATE OF NAPHTHVALENE AND ITS PHOTOCHEMISTRY: A QUALITATIVE AND QUANTITATIVE THEORETICAL INVESTIGATION[†]

E. AMITAI HALEVI

Department of Chemistry, Technion, Israel Institute of Technology, Haifa 32000 (Israel)

WALTER THIEL

Theoretische Chemie, Bergische Universität, Gesamthochschule Wuppertal, D-5600 Wuppertal 1 (F.R.G.)

(Received October 15, 1984)

Summary

Orbital correspondence analysis in maximum symmetry of the photoisomerization of naphthvalene to naphthalene, with predominant formation of its lowest triplet, is inconsistent with the assignment of the first excited singlet of naphthvalene to the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) state 1B_1 , suggesting instead that it is the totally symmetric open-shell singlet $^1A_1'$. Computations with modified neglect of diatomic overlap and the correlated version of modified neglect of diatomic overlap confirm that the HOMO and LUMO indeed have b_2 and a_2 symmetry respectively, but that the first-order configuration interaction stabilizes $^1A_1'$ sufficiently to bring it below 1B_1 . These results illustrate the value of orbital symmetry analysis of photochemical reactions as an aid in the characterization of the relevant excited states and the necessity, in the present instance, of including configuration interaction, even for the purposes of qualitative discussion.

1. Introduction

Two superficially unrelated questions are addressed in this paper.

(a) What predictions, if any, about the relative efficiency of the various reactions open to a photoexcited molecule can be based on an orbital symmetry analysis?

(b) How reliable are computations at the orbital level for ascertaining the energetic order of the lower excited states, and when is it necessary to include configuration interaction (CI) for this purpose?

[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

To our knowledge, the first attempt to deduce the nature of the lowest excited singlet of a molecule from its photochemistry on the basis of an orbital correlation diagram was made by Ramsey [1]. Although his analysis of the photolysis of polysilanes has been shown to be oversimplified [2], its principal conclusion — the absence of d orbital involvement in the lowest excited state — still stands [2].

This investigation is concerned with the photoisomerization of naphthvalene to naphthalene, for which Turro *et al.* [3] report the unexpected results summarized in Fig. 1. Like its lower homologue benzvalene, naphthvalene shows remarkable kinetic stability in its ground state, despite its high energy content. Photoexcitation presumably produces its first excited singlet, which fluoresces to its own ground state to the extent of about 10%. Of the remaining 90%, 20% are unaccounted for; this includes whatever non-radiative conversion to the ground state of naphthvalene and/or direct isomerization to the ground state of naphthalene may be taking place (ref. 3, footnote 12). The remaining 70% involve isomerization to electronically excited naphthalene, but S_1 , the expected product of reaction on the open-shell singlet surface, is conspicuously absent. Instead, the predominant process is the direct formation of the lowest triplet of naphthalene.

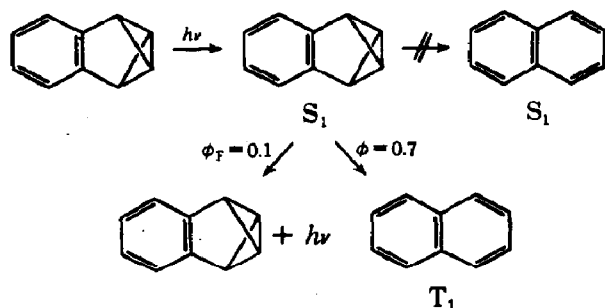


Fig. 1. The reactivity pattern of photoexcited naphthvalene [3].

2. Orbital correspondence analysis in maximum symmetry (OCAMS)

Figure 2 is the correspondence diagram [4 - 6] for the isomerization of naphthvalene to naphthalene. The molecular orbitals of the latter are stacked at the centre; in addition to the five π and two lowest π^* orbitals, they include three $\sigma(\text{C}-\text{C})$ and two $\sigma(\text{C}-\text{H})$ combinations. In all, these 12 molecular orbitals of naphthalene suffice to describe the behaviour of the 20 electrons which can be considered to be directly involved in its formation from naphthvalene. The remaining 28 valence electrons occupy molecular orbitals which remain substantially unaffected by the isomerization. The energetic ordering of the molecular orbitals is unimportant, except for those which are singly occupied in the relevant open-shell states. For convenience, the $\sigma(\text{C}-\text{H})$ combinations are placed at the bottom, the $\sigma(\text{C}-\text{C})$ orbitals

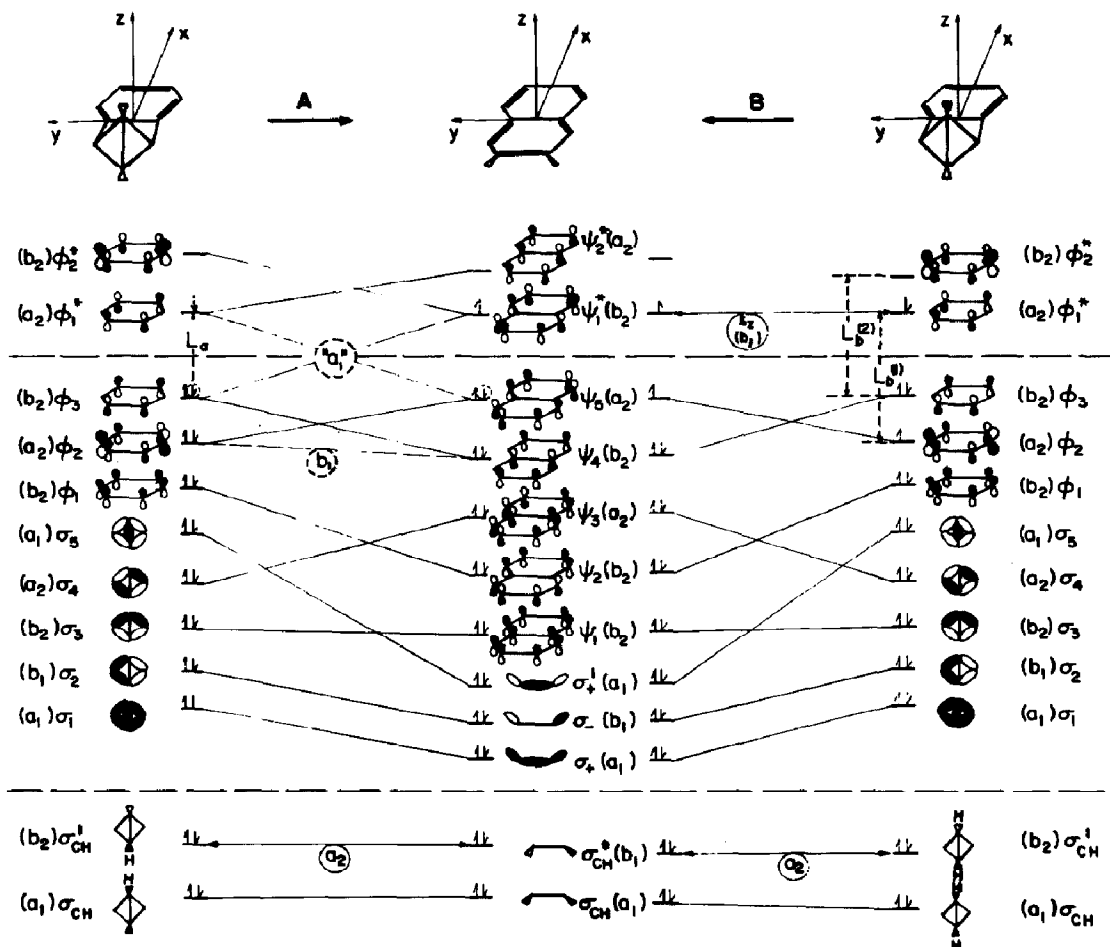


Fig. 2. OCAMS correspondence diagrams for the isomerization of naphthvalene to naphthalene: A, ground state isomerization (—) and ${}^1\text{B}_1(\text{naphthvalene}) \rightarrow {}^3\text{B}_1[{}^3\text{B}_{2u}](\text{naphthalene})$ (---); B, ${}^1\text{A}_1'(\text{naphthvalene}) \rightarrow {}^3\text{B}_1[{}^3\text{B}_{2u}](\text{naphthalene})$ (see text).

are placed above them and then the π and π^* orbitals are located in their familiar sequence [7]. Each is labelled according to its irreducible representation in C_{2v} , the symmetry point group of naphthvalene and thus the group of highest common symmetry, with the C_2 axis specified to lie along x . In D_{2h} , to which naphthalene properly belongs, its lowest triplet is ${}^3\text{B}_{2u}$ (ref. 8, p. 284), derived from the highest occupied molecular orbital \rightarrow lowest unoccupied molecular orbital (HOMO \rightarrow LUMO) excitation, which is labelled ${}^3\text{B}_1$ in C_{2v} , as shown. Its lowest open-shell singlet is known to be ${}^1\text{B}_{3u}$ (ref. 8, p. 70). In C_{2v} it is labelled ${}^1\text{A}_1'$ to distinguish it from the closed-shell ground state ${}^1\text{A}_1$. ${}^1\text{A}_1'$ is the lower of two totally symmetric open-shell states which is stabilized, as its partner is destabilized, by interaction between the two next-lowest configurations [... $a_u b_{3g}$] and [... $b_{1u} b_{2g}$] [9] which map onto [... $a_2 a_2$] and [... $b_2 b_2$] respectively in C_{2v}^x .

The 12 relevant orbitals of naphthvalene are listed on each side of Fig. 2. Reading upward, they are the in-phase and out-of-phase combinations of the two C—H bond orbitals, the five σ (C—C) orbitals which make up the skeleton of the bicyclobutane moiety, and the three π and two lower-lying π^* orbitals of the benzene ring. The degeneracies of the benzene MOs are assumed to be split as shown because two of the π orbitals map onto the same representation (b_2) of C_{2v} , whereas two π^* orbitals (the upper is not included in Fig. 2) map onto a_2 . Gleiter *et al.* [10] have shown by photoelectron spectroscopy that this splitting is quite large, as a result of the interaction between the bicyclobutane moiety and the aromatic π system.

2.1. Isomerization on the ground state surface

Figure 2 treats the isomerization as a 20-electron problem, so that the 10 lowest molecular orbitals of the reactant (naphthvalene) and the product (naphthalene) must each be doubly occupied in the closed-shell ground states. On the left-hand side of Fig. 2 correlation lines are drawn between orbitals which have the same irreducible representation in C_{2v} . When only the C—C orbitals are considered the ground state isomerization appears to be allowed, since all eight occupied orbitals of naphthvalene correspond directly to occupied orbitals of naphthalene. Naphthvalene might therefore be expected to isomerize easily, but as noted it is remarkably stable.

The similarly unexpected kinetic stability of benzvalene has raised doubts about the reliability of orbital symmetry conservation as a criterion for selecting energetically favourable reaction pathways [11]. An attempt to resolve these doubts has been made previously [6]; they can be dispelled entirely if the σ (C—H) orbitals are considered explicitly, as they are at the bottom of Fig. 2, while retaining the intuitive conviction of virtually all chemists that the electron pair constituting each C—H bond remains localized in it as the two nuclei bonded by it move through space [12]. One of the two such combinations in the reactant (b_2) is converted in the product to one of symmetry species b_1 . This can be done by motion along a twisting coordinate a_2 , which retains axial symmetry; as a result the reacting molecule is desymmetrized from C_{2v} to C_2 , the subgroup which is the kernel of a_2 [5]. The C—C bonding orbitals, which were in full pairwise correlation in C_{2v} , cannot choose but remain in correlation in C_2 , as they would in any other subgroup of C_{2v} , but they provide no driving force for the isomerization as they do in the classical polyene cyclizations for example (the polyene cyclizations are exemplified by their simplest member allyl-cyclopropyl) [12].

2.2. Photophysics and photochemistry

We assume that the relaxation processes noted in Fig. 1 originate in S_1 of naphthvalene. On the left-hand side of Fig. 2 the *a priori* reasonable assumption is made that it is 1B_1 which, like T_1 , is derived from the HOMO-LUMO or L_a , configuration [... b_2a_2]. However, the alternative possibility that, as in naphthalene or benzene itself (ref. 8, p. 70), the L_b singlet is the more stable, despite the orbital sequence in the ground state, cannot be sum-

marily dismissed. If ${}^1A_1'$ is indeed S_1 , calculations at the molecular orbital level will inevitably produce misleading results and the inclusion of CI is essential even for the purposes of qualitative discussion of the photochemistry. This alternative is depicted on the right-hand side of Fig. 2; one of the two contributing configurations [... a_2a_2] is shown explicitly and the second [... b_2b_2] is implied.

The dominant process, reactive intersystem crossing from S_1 (naphthvalene) to T_1 (naphthalene), can be dealt with by means of an extension of orbital correspondence analysis in maximum symmetry (OCAMS) to spin non-conservative processes [13]. Loosely speaking, for such a transition to occur the unit of spin angular momentum acquired by the triplet must be compensated by a unit of orbital angular momentum about the same axis. In an abelian group this requirement leads to the condition that spin flip can be induced by any one of the three spin factors s_x , s_y or s_z in the spin-orbit operator, provided that the corresponding orbital factor l_x , l_y or l_z has the proper symmetry to induce a one-electron correspondence between a reactant r and a product p orbital:

$$\gamma(r) \times \gamma(p) = \gamma(l_x), \gamma(l_y) \text{ or } \gamma(l_z)$$

The orbital factors l_x , l_y and l_z behave like rotations about the three cartesian axis, as do the corresponding spin factors. In C_{2v}^x , R_x , R_y and R_z transform as a_2 , b_2 and b_1 respectively. Most importantly there is no totally symmetric (a_1) rotation, so that the spin of an electron cannot be flipped as it passes between two orbitals which have the same irreducible representation.

It is clear from A of Fig. 2 that each of the two unpaired electrons is transferred between orbitals which have the same symmetry label; the spin flip is "forbidden". Moreover the in-plane (b_1) distortion, which is called for in order to induce the two-electron correspondence between $\phi_2(a_2)$ and $\psi_4(b_2)$, compounds the "forbiddenness". If S_1 of naphthvalene is 1B_1 , its predominant crossing to 3B_1 (naphthalene) is inexplicable.

In sharp contrast, B of Fig. 2 shows that ${}^1A_1'$ can be converted to the z component of T_1 (naphthalene), because one of the two one-electron correspondences is direct ($\phi_2(a_2) \leftrightarrow \psi_5(a_2)$) whereas the other ($\phi_1^*(a_2) \leftrightarrow \psi_1^*(b_2)$) is induced by l_z , which can be interpreted as arising out of a transient ring current about the z axis, *i.e.* in the plane of the aromatic ring. We note further that there is no need for a gratuitous in-plane distortion; all of the two-electron correspondences are now direct. Excitation of the geometrically necessary a_1 and a_2 modes is sufficient.

The analysis just completed compels the conclusion that the totally symmetric configuration [... a_2a_2] contributes substantially to the first excited singlet of naphthvalene. Since, as already pointed out, $\phi_2(a_2)$ lies below $\phi_3(b_2)$ in the ground state of the molecule, the only reasonable explanation is that interaction with at least one other totally symmetric configuration, presumably [... b_2b_2] brings ${}^1A_1'$ below 1B_1 .

The remaining features of the reactivity pattern of photoexcited naphthvalene (Fig. 1) are also consistent with the assignment of ${}^1A_1'$ to its lowest excited singlet.

Fluorescence from ${}^1A_1'$ is derived from the formally forbidden fluorescence from S_1 (${}^1B_{3u}$) of benzene but is allowed in the lowered symmetry of naphthvalene by a longitudinally polarized transition moment. A very recent spectroscopic study of naphthvalene [14] identifies the lowest frequency absorption as L_b and finds its intensity to be enhanced relative to benzene (ref. 8, p. 70), so that appreciable fluorescence would not be unexpected although its extent would depend on the relative efficiency of competing relaxation processes.

At first sight the apparent failure of S_1 to react along the open-shell surface is surprising; since the first excited states of naphthvalene and naphthalene are both totally symmetric, their interconversion should be rapid. However, S_0 of naphthalene is also totally symmetric, a circumstance that contributes to the efficient quenching of the fluorescence of photoexcited naphthalene (ref. 8, p. 178), presumably by internal conversion. As noted above the highest symmetry pathway consistent with the geometric requirements of the isomerization must have an a_2 component. The reaction coordinate will therefore be a superposition of a_1 and a_2 symmetry coordinates, so that the product naphthalene will necessarily be vibrationally excited in modes of these symmetry species. In consequence, it should be no surprise that internal conversion of vibrationally excited S_1 to S_0 is effective enough to override the naphthalene fluorescence entirely. The fact that the experimental results allow no more than 20% to the inherently facile non-radiative sequence $S_1(\text{naphthvalene}) \rightarrow S_1(\text{naphthalene}) \rightarrow S_0(\text{naphthalene})$ (ref. 3, footnote 12) attests to an extremely efficient mechanism for the predominant intersystem crossing to T_1 ; presumably this is the OCAMS-allowed generation of its z component under the influence of a transient ring current in the aromatic π system (see above).

3. Calculations on the excited states of naphthvalene

The qualitative conclusions drawn above were examined quantitatively by modified neglect of diatomic overlap (MNDO) [15] and the correlated version of modified neglect of diatomic overlap (MNDOC) [16] calculations for naphthvalene at its MNDO-optimized ground state geometry. In this study both semi-empirical methods lead to completely analogous predictions, so that it seems sufficient to concentrate on one set of results. Since MNDOC is known to be more accurate than MNDO for excited states [17], we shall only present the MNDOC results.

Table 1 lists the MNDOC energies of the four low-lying configurations of naphthvalene which arise from single excitations involving the two highest occupied and the two lowest unoccupied molecular orbitals. As expected at the orbital level, the lowest energy singlet configuration is B_1 , which is

TABLE 1

Correlated version of modified neglect of diatomic overlap energies of the lowest excited singlet configurations of naphthvalene^a

No.	Symmetry	Excitation ^b	E (eV)
1	B ₁	$\phi_3(b_2) \rightarrow \phi_1^*(a_2)$	4.96
2	A ₁	$\phi_3(b_2) \rightarrow \phi_2^*(b_2)$	5.11
3	A ₁	$\phi_2(a_2) \rightarrow \phi_1^*(a_2)$	5.22
4	B ₁	$\phi_2(a_2) \rightarrow \phi_2^*(b_2)$	5.55

^aRelative to the ground state self-consistent field energy.

^bSee Fig. 2.

produced by the HOMO → LUMO excitation $\phi_3(b_2) \rightarrow \phi_1^*(a_2)$. The other three configurations, however, are only slightly higher in energy; this is not too surprising in view of the correlation of the relevant MOs in naphthvalene with the degenerate e_{1g} and e_{2u} MOs of benzene.

Closer inspection of Table 1 shows that the two totally symmetric open-shell configurations are almost degenerate, so that CI cannot be neglected. Inclusion of the first-order 2×2 CI causes a much larger split in the case of the A₁ states than in those of B₁ symmetry, so that the lowest excited singlet is now ¹A₁'. This ¹A₁'–¹B₁ inversion is confirmed by a full CI calculation in an active space defined by the two highest occupied and the two lowest unoccupied molecular orbitals. At this full CI level the lowest excited singlet is also of A₁ symmetry and lies 0.68 eV below the first ¹B₁ state (see Table 2). Also listed in Table 2 are the results of the recent investigation referred to above [14] in which the excited singlet states of naphthvalene were observed by linear dichroic absorption spectroscopy and

TABLE 2

Correlated version of modified neglect of diatomic overlap–configuration interaction energies of the lowest excited singlet states of naphthvalene

No.	State label	E (eV)		
		First-order CI ^a	Full CI ^b	Experimental ^c
1	¹ A ₁ '	4.14	4.07	4.46
2	¹ B ₁	4.32	4.75	5.27
3	¹ A ₁ ''	6.19	4.87	—
4	¹ B ₁ '	6.19	6.19	—

^a 2×2 CI of the symmetry-adapted configurations listed in Table 1. The energies are given relative to the ground state self-consistent field energy.

^bCI space of 12 configurations for the A₁ singlets and of eight configurations for the B₁ singlets (see text). The energies are given relative to the ground state CI energy.

^cFrom ref. 14. The calculated CNDO–CI energies are 4.23 eV for ¹A₁' and 4.86 eV for ¹B₁.

assigned with the aid of complete neglect of diatomic overlap-configuration interaction (CNDO-CI) calculations. In agreement with our present results, the lowest excited singlet was found to be of A_1 symmetry with an observed ${}^1A_1' - {}^1B_1$ gap of 0.81 eV. As expected [17] MNDOC underestimates the measured vertical excitation energies but reproduces their separation quite well (see Table 2).

These results thus demonstrate that a one-configuration description of naphthvalene photochemistry is misleading because the lowest energy excited configuration (1B_1 , HOMO→LUMO excitation) does not correspond to the lowest excited state ${}^1A_1'$. As in the analogous case of naphthalene [9], the sequence of excited states is determined by first-order CI effects. Hence, even for a qualitative understanding of naphthvalene photochemistry, it is necessary to go beyond the orbital level and include CI.

An alternative purely energetic rationalization of the photochemical reactivity pattern might be that the triplet of naphthalene is the only accessible excited state (the excited singlet states lie above S_1 (naphthvalene)). It can be excluded as follows. MNDO places benzvalene 80.3 kcal mol⁻¹ above benzene, whereas the experimental energy difference is 67.5 kcal mol⁻¹ [18]. Correcting the corresponding calculated energy difference between naphthvalene and naphthalene (69.0 kcal mol⁻¹) by the "MNDO error" of 12.8 kcal mol⁻¹ yields 56.2 kcal mol⁻¹ (2.44 eV) as the "best" estimate of the difference between the ground state energies of naphthvalene and naphthalene. The experimental results, as cited in Table 2, thus place ${}^1A_1'$ (naphthvalene) 6.90 eV above the ground state of naphthalene, *i.e.* far above not only the first excited singlet of naphthalene (${}^1B_{3u}$, 3.87 eV) but also above a number of its higher singlets [19].

4. Conclusions

We have demonstrated that orbital symmetry correlation diagrams, specifically when treated by the OCAMS procedure [4 - 6], are applicable to the analysis of photochemical reactions. In the present instance the predominant conversion of photoexcited naphthvalene to the lowest triplet of naphthalene can be rationalized only if the first excited state of the former is identified as ${}^1A_1'$, rather than as the HOMO-LUMO state 1B_1 . This assignment, which is also compatible with the other features of the reactivity pattern illustrated in Fig. 1 and has recently been established spectroscopically [14] is confirmed by MNDOC-CI calculations. Our computations emphasize the necessity of including CI when dealing with the photochemistry of aromatic molecules, even those which are strongly perturbed by π - σ interactions, but suggest that first-order CI may be sufficient for the purposes of qualitative discussion.

Acknowledgments

We acknowledge support to E.A.H. from the Fund for Promotion of Research at Technion and to W.T. from the Fonds der Chemischen Industrie. Thanks are due to Professor R. Gleiter and Professor S. Speiser for valuable discussions.

References

- 1 B. G. Ramsey, *J. Organomet., Chem.*, **67** (1974) C67.
- 2 E. A. Halevi, G. Winkelhofer, N. Meisl and R. Janoschek, to be published.
- 3 N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnahan and T. J. Katz, *J. Am. Chem. Soc.*, **95** (1973) 2035.
- 4 E. A. Halevi, *Helv. Chim. Acta*, **58** (1975) 2136.
- 5 J. Katriel and E. A. Halevi, *Theor. Chim. Acta*, **40** (1975) 1.
- 6 E. A. Halevi, *Nouv. J. Chim.*, **1** (1977) 229.
- 7 E. Heilbronner and H. Bock, *The HMO Model*, Vol. 3, Verlag Chemie, Weinheim, 1976, p. 120.
- 8 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970.
- 9 F. A. Cotton, *Chemical Applications of Group Theory*, Wiley, New York, 2nd edn., 1971, pp. 165 - 170.
- 10 R. Gleiter, K. Gubernator, M. Eckert-Maksic, J. Spanget-Larsen, B. Bianco, G. Gandillon and U. Burger, *Helv. Chim. Acta*, **64** (1981) 1312.
- 11 J. J. C. Mulder, *J. Am. Chem. Soc.*, **99** (1977) 5177.
- 12 E. A. Halevi, J. Katriel, R. Pauncz, F. A. Matsen and T. L. Welsher, *J. Am. Chem. Soc.*, **100** (1978) 359.
- 13 E. A. Halevi and C. Trindle, *Isr. J. Chem.*, **16** (1977) 283.
- 14 J. Spanget-Larsen, K. Gubernator, R. Gleiter, E. W. Thulstrup, B. Bianco, G. Gandillon and U. Burger, *Helv. Chim. Acta*, **66** (1983) 676.
- 15 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99** (1977) 4899, 4907.
- 16 W. Thiel, *J. Am. Chem. Soc.*, **103** (1981) 1413, 1420.
- 17 A. Schweig and W. Thiel, *J. Am. Chem. Soc.*, **103** (1981) 1425.
- 18 N. J. Turro, C. A. Renner and T. J. Katz, *Tetrahedron Lett.*, (1976) 4133.
- 19 *UV-Atlas of Organic Compounds*, Vol. 2, Butterworths, London, 1966.