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Transformation matrices as tool to investigate the changes in the electronic structure of reacting molecules along the reaction coordinate

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The calculation of the transformation matrix between the molecular orbitals of the transition state and the educt provides detailed information on the alteration and interaction of the MO's along the reaction coordinate. This is demonstrated for four different kinds of reactions: (a) Conrotatory ring-opening of cyclobutene; (b) Addition of methylene to ethylene; (c) Nucleophilic substitution of CH_3CN and CH_3NC by CN^-; (d) 1,2 Rearrangement of methylcarbene to ethylene. MNDO has been employed for the calculations but any other method may be used as well.

Key words: Transformation matrix—electronic structure of transition states—orbital interaction—reaction mechanism

1. Introduction

The reaction course of chemical reactions is frequently discussed and understood in terms of the molecular orbitals of the reacting species. Especially the frontier orbitals [1–4] are known to play a special role and it was concluded that the reaction course of a majority of chemical reactions is controlled by maximum HOMO-LUMO interaction [1]. On the other hand, it is known that reactions not only may be charge controlled [4], but also that subjacent orbitals may have a dominant influence [5]. All these theories are, of course, only valid for kinetically controlled reactions. In using these models, the MO's of the educts are usually taken for a perturbational treatment [4], a method which is valid only in the beginning of the reaction. However, the crucial point of a kinetically controlled reaction is the transition state and it is only assumed that the results from the stadium of beginning are indicative for the transition state. Some relationship is expressed in Fukui's so-called three principles [2] which state that along the reaction coordinate there is (a) a narrowing of the inter-frontier level separation; (b) a growing frontier electron density and (c) a co-operation of sub-principles and the general orientation and stereoselection rule. Thus, it is desirable to investigate the structure of transition states in terms of the educts to gain exact information how they are related to each other. The need for a new conceptual approach considering the whole potential energy surface has been recognized by Epiotis [6], who introduced a many-determinant reaction model.

It is the aim of this paper to investigate the electronic structure of the transition state in terms of the orbitals of the educts. This is easily done by calculating the transformation matrix between the MO coefficients of the educt and the transition state. Such a method, which uses the transformation matrix between species of *different* geometries, has successfully been employed to study the changes in the electronic structure of some organic molecules upon ionization [7].

2. Details of calculation

MNDO [8] calculations have been performed with optimization of all geometrical parameters. Transition states have been located as species with only one negative eigenvalue of the Hessian matrix by minimization of the gradient norm [9], with the exception of the nucleophilic substitution reactions. Here, equal distances between the cyano groups and the methyl–carbon atom have been assumed.

The matrix of the eigenvector of the transition state C_{TS} is expressed from the eigenvector matrix C_{E} of the corresponding educt by the transformation matrix T:

$$C_{\mathrm{TS}} = C_{\mathrm{E}} T$$

$$C_{\mathrm{E}}^{-1} C_{\mathrm{TS}} = T.$$

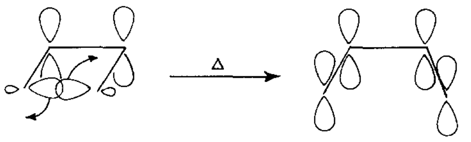
As C is a unitary matrix, its inverse is equal to the transposed and is easily constructed. If there were no changes in the electronic structure, T would be the unity matrix. For bimolecular reactions, the educt has been calculated as a "supermolecule" with a long distance between the reacting species (~8 Å), which reproduced the electronic structure of the two subsystems exactly the same as in separate calculations. There is an essential point which has to be stressed: Since T connects the electronic structures of species with different geometries, the result will be affected by the way how these geometries are placed in the coordinate system. We have solved this problem in the following way. Starting with the geometrical arrangement of the educt, a suitable variable was changed stepwise with complete optimization of all other geometrical variables, until the value of the transition state geometry was reached. With this placement in the coordinate system, the transition-state search routine was started and the geometry of the saddle point was determined. The electronic structure found in this way was used to construct C_{TS}. Since the choice of the geometrical variable and the position in the coordinate system is somewhat arbitrary, we checked the results by choosing different variables and coordinate arrangements. E.g. for the conrotatory ring-opening reaction of cyclobutene, we determined T calculating C_{TS} by choosing (a) the C_3—C_4 bond length as reaction coordinate, putting C_1 in the origin and C_1—C_2 along the x axis, and (b) the $C_1C_2C_3$ bond angle as reaction coordinate with C_1—C_2 along the y axis and C_1 in the origin; the ring was placed in both cases in the xy plane. Except for rounding errors, the result for T was the same.

3. Results and discussion

Tables 1 and 2 show the calculated geometries and heats of formation of educts and transition states. Table 3 lists the transformation matrices. The MO's of the transition states are in rows, the MO's of the educts in columns. The most important orbitals of the educts discussed in this paper whose shapes are not directly obvious are shown in Fig. 1.

3.1. Conrotatory ring opening of cyclobutene

The ring opening reaction of cyclobutene to butadiene is one of the "classical" examples of a pericyclic reaction and many theoretical investigations have been devoted to it [10–12].



(1)

The method of minimizing the gradient norm for locating a transition state [11] was demonstrated using reaction (1) as example. Our MNDO results for the transition state geometry and activation barrier are very similar to those [11] based upon MINDO/2 [13].

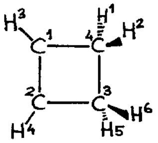
Regarding the symmetry of the orbitals, reaction (1) can be classified as thermal allowed ($\pi 2s + \sigma 2a$) cycloaddition of the opening C_3—C_4 σ-bond to the π-bond [14]. The appropriate MO's should therefore be dominating in the transition state.

Table 1. Heats of formation of the educts $\Delta H_f(E)$ and transition states $\Delta H_f(\mathrm{TS})$ and activation energies E_a in kcal/mol for reactions (1)–(5)

	Reaction				
	(1)	(2)	(3)	(4)	(5)
$\Delta H_f(\mathrm{E})$	31.0	122.7	72.0	113.4	88.5
$\Delta H_f(\mathrm{TS})$	80.7	128.6	94.5	146.1	110.4
E_a	49.7	5.9	22.5	32.7	21.9

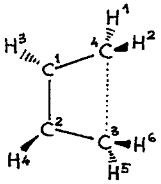
Table 2a–e. Bond lengths (Å) A—B, bond angles A—B—C and dihedral angles A—B—C—D (°) of educt (top) and transition state (bottom) for: **a** reaction (1); **b** reaction (2); **c** reaction (3); **d** reaction (4); **e** reaction (5)

a



C^4-C^1	1.52
C^1-C^2	1.35
C^4-H^1	1.10
C^1-H^3	1.07
C^4-C^3	1.57

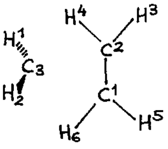
$C^4-C^1-C^2$	94.0°	$C^1-C^2-C^3-C^4$	0.3°
$H^1-C^4-C^1$	115.4°	$H^1-C^4-C^1-C^2$	244.3°
$H^3-C^1-C^2$	135.9°	$H^6-C^3-C^2-C^1$	244.3°



C^4-C^1	1.42
C^1-C^2	1.40
C^4-H^1	1.09
C^1-H^3	1.08
C^4-C^3	2.13

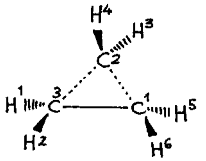
$C^4-C^1-C^2$	103.5°	$C^4-C^1-C^2-C^3$	21.6°
$H^1-C^4-C^1$	121.2°	$H^1-C^4-C^1-C^2$	217.6°
$H^3-C^1-C^2$	128.9°	$H^6-C^3-C^2-C^1$	217.6°
		$H^5-C^3-C^2-C^1$	60.6°

b



C^1-C^2	1.33
C^2-C^3	8.00
C^3-H^1	1.09
C^2-H^3	1.09

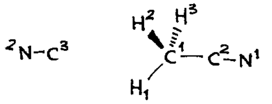
$H^1-C^3-H^2$	111.1°	$H^3-C^2-C^1-H^5$	0.0°



C^1-C^2	1.34
C^2-C^3	2.35
C^1-C^3	2.69
C^3-H^1	1.09
C^2-H^3	1.09

$C^3-C^2-C^1$	89.1°	$H^1-C^3-C^2-C^1$	60.7°
$H^1-C^3-H^2$	111.4°	$H^3-C^2-C^3-C^1$	−123.1°
		$H^3-C^2-C^1-H^5$	2.7°

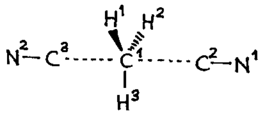
c



C^1-C^2	1.45
C^2-N^1	1.16
C^1-H	1.11
C^1-C^3	8.00
C^3-N^2	1.18

$C^1-C^2-N^1$	180.0
$H^1-C^1-H^2$	108.4°
$C^1-C^3-N^2$	180.0

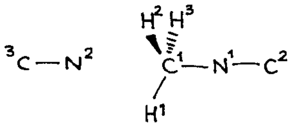
Table 2 (continued).



C^1-C^2	1.73
C^2-N^1	1.17
C^1-H	1.12
C^1-C^3	1.73
C^3-N^2	1.17

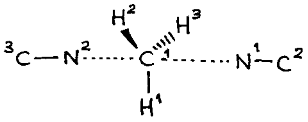
$C^1-C^2-N^1$	180.0
$H^1-C^1-H^2$	120.1°
$C^1-C^3-N^2$	180.0

d



C^1-N^1	1.43
N^1-C^2	1.19
C^1-H	1.11
C^1-N^2	8.00
N^2-C^3	1.18

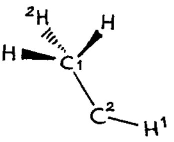
$C^1-N^1-C^2$	180.0
$H^1-C^1-H^2$	108.9°
$C^1-N^2-C^3$	180.0



C^1-N^1	1.76
N^1-C^2	1.18
C^1-H	1.11
C^1-N^2	1.76
N^2-C^3	1.18

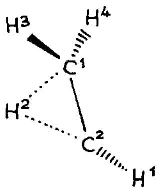
$C^1-N^1-C^2$	180.0
$H^1-C^1-H^2$	120.0°
$C^1-N^2-C^3$	180.0

e



C^1-C^2	1.46
C^2-H^1	1.09
C^1-H^2	1.11

$C^1-C^2-H^1$	119.6°	$H^2-C^1-C^2-H^1$	−91.5°
$C^2-C^1-H^2$	107.5°		



C^1-C^2	1.38
C^2-H^1	1.07
C^1-H^2	1.32
C^2-H^2	1.40

$C^1-C^2-H^1$	131.0°	$H^2-C^1-C^2-H^1$	−101.3°
$C^2-C^1-H^2$	62.7°	$H^3-C^1-C^2-H^1$	170.6°
$C^2-C^1-H^3$	121.4°	$H^4-C^1-C^2-H^1$	12.6°

Table 3a–e. Transformation matrix between the MO's of the educt (columns) and transition state (rows) and eigenvalues of the occupied MO's ε_i (eV) for: **a** reaction (1); **b** reaction (2): $(A) = C_2H_4$, $(B) = CH_2$; **c** reaction (3): $(A) = CH_3CN$, $(B) = CN^-$; **d** reaction (4): $(A) = CH_3NC$, $(B) = CN^-$; **e** reaction (5)

		Cyclobutene											
No.		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12
	ε_i	−41.76	−27.36	−26.51	−19.44	−16.65	−15.52	−13.62	−13.00	−12.26	−11.95	−9.77	
		$3A_1$	$4A_1$	$3B_2$	$4B_2$	$5A_1$	$1B_1$	$6A_1$	$1A_2$	$7A_1$	$5B_2$	$2B_1$	$2A_2$
1	−40.26	-.99	.08	-.00	-.00	-.03	-.01	.03	-.00	-.02	.00	.03	-.01
2	−29.18	-.01	-.01	.98	-.01	.02	.01	-.00	.01	-.03	.07	-.05	.03
3	−25.28	-.07	-.93	-.02	-.02	-.06	.04	.04	.04	-.13	.02	.05	-.03
4	−19.84	.00	.00	.02	.97	-.00	.18	.06	.04	-.05	.09	.07	-.03
5	−16.37	-.02	-.05	-.01	-.00	.94	-.00	-.09	.23	.03	.00	.09	-.03
6	−14.78	.00	-.03	-.06	.18	.01	-.90	.01	.02	-.03	.13	-.04	-.00
7	−14.59	-.03	-.02	-.01	.04	-.20	.04	-.75	.57	.13	-.06	-.09	.05
8	−13.37	.02	-.03	.10	.10	-.04	-.15	.01	-.05	.11	-.91	.28	-.10
9	−12.98	.01	-.01	.02	-.04	-.13	-.03	.58	.62	.48	.06	.02	.02
10	−9.56	-.01	-.07	.01	.07	.03	-.10	.06	.01	-.01	-.21	-.84	-.05
11	−9.05	-.01	-.12	-.00	.07	-.01	.04	-.14	-.40	.65	.09	-.01	.43
12		.04	-.03	.10	-.04	-.11	-.26	-.13	.04	-.01	.21	.39	.00
13		-.01	-.03	.04	.00	-.02	-.00	-.15	-.17	.37	.16	-.05	-.85
14		-.04	-.03	-.03	-.02	.10	.03	.01	-.06	.29	-.06	.05	-.11
15		.02	.02	-.08	.05	-.05	.10	-.04	.02	-.00	.04	-.04	.00
16		-.01	-.01	-.01	.03	.03	-.11	-.06	-.05	.03	.01	-.02	.06
17		-.03	-.05	.03	.02	.10	-.08	-.04	-.15	.19	-.01	-.06	.14
18		.01	.03	.06	-.08	-.04	-.00	-.00	.05	-.04	-.02	-.03	.00
19		-.04	-.05	-.00	.01	.08	-.00	-.07	.06	.20	-.05	-.06	.15
20		-.03	-.00	.02	.04	.09	-.00	-.02	-.02	-.03	-.01	-.10	.11
21		-.02	-.06	.02	.02	.04	-.08	-.01	-.01	.02	-.03	-.03	.04
22		.00	-.01	-.05	-.01	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

No.		(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22
	ε_i										
		$6B_2$	$3B_1$	$8A_1$	$7B_2$	$3A_2$	$8B_2$	$8A_1$	$9A_1$	$9B_2$	$10B_2$
1	−40.26	-.03	-.02	.02	-.03	.04	.01	-.01	.02	.01	-.01
2	−29.18	.13	-.03	.04	-.03	-.02	-.00	.02	-.00	.07	.05
3	−25.28	.04	.02	.02	-.02	-.01	-.02	-.02	.03	-.00	-.04
4	−19.84	-.09	.06	-.01	-.01	-.04	-.00	.00	-.01	.00	-.03
5	−16.37	-.06	-.04	.05	-.08	.14	.02	-.02	.08	.04	-.02
6	−14.78	.27	.12	.08	-.12	-.02	.09	.00	.00	.05	.08
7	−14.59	.06	.07	-.01	.03	-.01	.03	.07	.11	.02	.07
8	−13.37	-.00	-.07	.01	-.04	.10	-.01	-.06	.04	-.04	-.03
9	−12.98	-.00	-.03	-.06	.04	.09	-.06	-.01	.08	-.05	-.05
10	−9.56	-.38	-.22	.15	.01	.01	.07	-.00	.03	.02	-.00
11	−9.05	-.03	.03	.20	-.14	.33	.08	.03	.09	.02	.09
12		-.67	-.44	.10	.03	-.05	.06	-.06	-.05	-.18	-.01
13		.03	.02	-.10	.01	.15	-.04	-.11	-.04	-.10	.00
14		.02	.01	.33	.00	-.73	-.00	.49	-.04	.04	-.03
15		.37	-.69	-.07	-.58	-.04	-.11	-.01	-.03	.03	-.10
16		-.04	-.07	.04	.21	.03	-.94	.01	.01	.17	.10
17		-.08	-.02	-.70	.03	-.42	.02	-.22	.41	-.02	.04
18		-.31	.49	-.04	-.72	-.06	-.25	-.00	-.04	-.21	-.15
19		.03	.03	-.07	.05	-.23	.01	-.46	-.79	.00	.03
20		.21	-.05	.05	.15	-.01	-.11	.06	.01	-.93	.09
21		-.09	-.04	-.54	.01	.24	.02	.68	-.40	.00	.03
22		-.07	-.00	.01	-.19	-.04	.04	-.00	.00	.03	.96

		$CH_2+C_2H_4$											
No.		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12
	ε_i	−35.28	−26.86	−22.62	−15.80	−14.57	−14.20	−12.61	−10.15	−9.13			
		$2A_g(A)$	$2A_1(B)$	$2A_u(A)$	$1B_{3u}(A)$	$3A_g(A)$	$1B_2(B)$	$1B_{2g}(A)$	$1B_{2u}(A)$	$3A_1(B)$	$1B_1(B)$	$1B_{3g}(A)$	$2B_{3u}(A)$
1	−35.60	.99	.16	.00	-.00	-.00	.00	-.00	.01	-.03	-.04	-.00	-.00
2	−26.54	.16	-.98	-.10	.00	-.00	-.00	-.00	-.07	.00	-.00	-.02	.00
3	−22.74	-.01	.10	-.99	-.00	.01	.00	-.00	.02	.05	.01	.01	-.00
4	−15.92	-.00	-.00	-.00	-.99	.00	-.14	-.01	-.00	.00	-.00	-.00	-.00
5	−14.69	-.00	.00	-.01	-.00	-1.00	.00	-.00	.03	.02	-.01	.01	-.00
6	−14.00	-.00	.00	-.00	.14	-.00	-.99	.07	.00	.00	-.00	.00	-.00
7	−12.73	-.00	.00	.00	.02	.00	-.06	-1.00	.00	.00	-.00	.00	.00
8	−10.61	-.01	-.07	-.01	-.00	.02	-.00	.00	.89	-.42	-.14	.02	-.00
9	−8.64	-.03	.03	-.05	.00	-.03	-.00	-.00	-.40	-.90	.12	.12	.00
10		-.04	.00	-.01	.00	.01	.00	.00	-.15	-.01	-.92	.35	-.00
11		-.02	.02	-.02	.00	-.01	.00	-.00	-.09	-.12	-.34	-.93	.00
12		.00	.00	.00	.00	.00	.00	-.00	-.00	.00	.00	-.00	-1.00
13		.00	-.00	.00	-.01	.00	-.00	.01	.00	-.00	.00	.00	-.03
14		.00	-.00	-.00	.00	-.00	-.00	-.00	.01	.01	-.00	-.02	-.00
15		-.00	.00	-.00	-.00	-.00	-.00	-.00	.01	-.01	-.01	.03	.00
16		-.00	-.00	.00	.00	.00	.00	-.01	-.00	-.00	.00	-.00	-.03
17		-.00	.00	-.00	.00	.00	-.00	.00	.01	-.02	-.04	.01	-.00
18		.00	-.00	-.01	-.00	-.00	.00	-.00	.00	.02	.02	-.02	.00

The transformation matrix shown in Table 3a fully supports the frontier MO (FMO) consideration, but there are some additional and unexpected details. The HOMO of the transition state mainly consists of the occupied MO 9 (C_3—C_4 σ-bonding) and the unoccupied LUMO (π^*). However, there are also large

Table 3 (continued).

No.	ε_i	(13)	(14)	(15)	(16)	(17)	(18
		$4A_1(B)$	$2B_2(B)$	$4A_g(A)$	$3A_u(A)$	$4A_u(A)$	$2B_{2g}(A)$
1	−35.60	-.00	-.00	.00	.00	.00	-.00
2	−26.54	.00	.00	-.00	-.00	-.00	.00
3	−22.74	-.00	.00	-.00	.00	-.00	.01
4	−15.92	.01	.00	.00	.00	-.00	.00
5	−14.69	-.00	.00	-.00	.00	-.00	.00
6	−14.00	.00	.00	-.00	.00	-.00	-.00
7	−12.73	-.01	.00	.00	-.01	-.00	.00
8	−10.61	.00	.01	.01	.00	.02	-.01
9	−8.64	.00	-.01	.01	.00	.00	-.02
10		-.00	.00	.03	.00	.04	-.02
11		-.00	.01	-.03	-.00	.01	.01
12		.03	.00	-.00	-.03	.00	-.00
13		-1.00	-.00	.00	-.02	-.00	.00
14		.00	-.94	.35	.00	.02	-.01
15		.00	-.35	-.93	-.00	.03	-.01
16		-.02	-.00	-.00	1.00	-.00	-.00
17		.00	-.05	-.07	-.00	-1.00	-.00
18		-.00	.02	.01	-.00	.00	-1.00

$CN^- + CH_3CN$

No.	ε_i	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12
		−37.17	−30.38	−28.16	−16.94	−13.83	−13.83	−12.67	−11.30	−11.30	−9.05	−4.86	−4.86
		$4A_1(A)$	$5A_1(A)$	$3\sigma(B)$	$6A_1(A)$	$1E(A)$	$1E'(A)$	$7A_1(A)$	$2E(A)$	$2E'(A)$	$4\sigma(B)$	$1\pi(B)$	$1\pi'(B)$
1	−32.46	-.66	-.13	-.72	.12	.00	-.00	.04	-.00	.00	-.03	-.00	.00
2	−31.37	.73	-.29	-.62	.01	.00	-.00	.01	-.00	.00	-.01	-.00	.00
3	−26.21	.10	.89	-.31	-.11	-.00	-.00	-.04	.00	.00	.21	.00	.00
4	−13.83	.12	.28	.04	.67	.00	-.00	-.02	-.00	.00	-.61	-.00	.00
5	−10.52	.00	.04	-.01	-.53	-.00	-.01	.47	.00	.00	-.66	-.00	.00
6	−10.21	-.00	-.00	.00	.00	-.69	-.59	-.00	.21	.18	.00	.18	.24
7	−10.21	-.00	-.00	.00	.00	.59	-.69	-.00	-.18	.21	.00	.24	-.18
8	−8.44	.04	.10	.02	.02	-.00	.00	.72	-.00	.00	.33	.00	-.00
9	−7.75	.00	.00	-.00	.00	.08	.39	.00	.08	.42	-.00	.78	.22
10	−7.75	.00	.00	.00	.00	.39	-.08	.00	.42	-.08	.00	-.22	.78
11	−7.26	-.00	-.00	.00	-.00	.06	.08	-.00	.50	.69	.00	-.39	-.33
12	−7.26	-.00	-.00	.00	.00	-.08	.05	.00	-.69	.50	.00	-.33	.39
13	−4.28	-.01	-.06	.02	.40	-.00	-.00	.48	.00	.00	.11	.00	.00
14		.00	-.00	.00	.00	-.02	.04	.00	.01	-.04	.00	-.04	.01
15		.00	.00	.00	-.00	.04	.02	-.00	-.04	-.01	-.00	-.01	-.04
16		-.00	.00	-.00	-.00	.04	-.05	-.00	.02	-.02	-.00	-.00	.00
17		.00	.00	-.00	-.00	.05	.04	-.00	.02	.02	-.00	.00	.00
18		.02	.11	-.04	-.25	-.00	.00	-.14	-.00	-.00	-.17	.00	-.00
19		.00	.00	-.00	.00	.04	-.04	.00	-.00	.00	-.00	-.01	.01
20		-.00	-.00	-.00	-.00	-.04	-.04	-.00	.00	.00	.00	-.01	-.01
21		-.04	-.04	.01	-.10	.00	.00	-.07	-.00	.00	.06	-.00	.00
22		.01	.04	-.01	-.04	.00	.00	-.01	-.00	.00	-.02	-.01	.00
23		-.01	.01	-.00	-.02	.00	.00	.01	-.00	-.00	.00	.00	-.00

No.	ε_i	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23
		−3.36										
		$5\sigma(B)$	$3E(A)$	$3E'(A)$	$8A_1(A)$	$4E(A)$	$4E'(A)$	$9A_1(A)$	$10A_1(A)$	$2\pi(B)$	$2\pi(B)$	$6\sigma(B)$
1	−32.46	.08	-.00	.00	-.01	.00	.00	-.01	.00	-.00	-.00	.01
2	−31.37	.00	.00	-.00	-.00	-.00	-.00	-.03	.01	-.00	-.00	-.00
3	−26.21	-.21	-.00	.00	-.05	.00	.00	.01	-.02	-.00	-.00	-.03
4	−13.83	.23	.00	-.00	-.05	.00	.00	-.17	.03	.00	.00	.02
5	−10.52	-.21	-.00	.00	-.13	.00	.00	-.01	-.02	-.00	-.00	-.01
6	−10.21	.00	.04	.04	.00	-.02	.02	-.00	.00	-.04	.06	.00
7	−10.21	.00	-.04	.04	.00	.02	.02	.00	.00	-.06	-.04	.00
8	−8.44	.58	.00	-.00	-.05	.00	.00	-.14	.01	.01	.00	.03
9	−7.75	.00	-.01	-.04	-.00	.01	-.03	.00	-.00	-.03	.01	.01
10	−7.75	.00	-.04	.01	.00	.03	.01	-.00	.00	.01	.03	-.00
11	−7.26	.00	-.02	-.02	-.00	-.00	.00	-.00	.00	-.01	.01	-.00
12	−7.26	.00	.02	-.02	.00	.00	.00	.00	-.00	-.01	-.01	-.00
13	−4.28	-.60	.00	-.00	.47	-.00	-.00	.10	.02	-.01	-.00	-.01
14		.01	-.00	.00	-.00	-.05	-.14	-.00	-.00	-.95	-.25	.00
15		.00	.00	.00	.00	.14	-.05	.00	.00	-.25	.95	-.00
16		.00	.63	-.76	.00	.10	.13	-.00	-.00	-.02	-.02	-.00
17		.00	.76	.63	.00	.13	-.10	.00	-.00	.02	-.03	-.00
18		.36	-.00	.00	.86	-.01	-.00	.06	.02	.00	-.00	-.10
19		-.00	.11	-.12	-.01	-.64	-.73	.00	-.00	.12	.09	-.00
20		-.00	-.12	-.11	.00	.73	-.64	-.00	.00	.09	-.12	.00
21		-.16	.00	.00	.13	-.01	-.00	-.95	.11	-.00	.00	.16
22		.03	.00	.00	.07	-.00	-.00	.19	.18	.00	.00	.96
23		-.00	.00	-.00	-.05	.00	.00	.07	.93	-.00	-.00	-.19

contributions from the occupied MO 8 and the unoccupied MO 17. Both MO's have π-symmetry and are located mainly at C_3 and C_4 as shown in Fig. 1. Due to their shapes, they may be more influenced by substituents at C_3 and C_4 and therefore, substituent effects may rather work via MO 17 and MO 8 than via the LUMO.

Table 3 (continued).

$CN^- + CH_3NC$

No.		⟨1⟩	⟨2⟩	⟨3⟩	⟨4⟩	⟨5⟩	⟨6⟩	⟨7⟩	⟨8⟩	⟨9⟩	⟨10⟩	⟨11⟩	⟨12
	ε_i	−36.88	−29.44	−28.14	−18.17	−14.14	−14.14	−10.97	−10.78	−10.78	−9.04	−4.85	−4.85
		$4A_1(A)$	$5A_1(A)$	$3\sigma(B)$	$6A_1(A)$	$1E(A)$	$1E'(A)$	$7A_1(A)$	$2E(A)$	$2E'(A)$	$4\sigma(B)$	$1\pi(B)$	$1\pi'(B)$
1	−31.77	.74	.03	−.65	.13	.00	−.00	−.03	−.00	.00	−.08	.00	−.00
2	−30.96	.63	−.32	.70	−.02	.00	.00	−.00	−.00	.00	.02	−.00	.00
3	−25.54	.16	.90	.28	.16	.00	.00	−.01	−.00	−.00	−.22	.00	.00
4	−14.32	−.14	−.23	.05	.68	.00	.00	.03	.00	.00	−.63	.00	.00
5	−10.66	−.00	.00	.00	.00	−.86	−.22	−.00	.34	−.03	.00	.25	−.10
6	−10.66	.00	−.00	.00	−.00	.22	−.86	−.00	−.03	−.34	−.00	−.10	−.25
7	−10.38	.01	−.02	−.02	−.60	−.01	−.00	−.35	−.00	.00	−.66	.00	−.00
8	−7.57	.00	.00	−.00	−.00	−.42	−.05	.01	−.56	.07	−.00	−.70	.09
9	−7.57	−.00	−.00	.00	−.00	−.05	.42	.00	−.07	−.56	−.00	−.09	−.70
10	−7.07	−.00	.00	.00	.00	.07	.09	−.01	.70	−.25	−.00	−.60	.26
11	−7.07	.00	.00	−.00	−.00	−.09	.07	.00	−.25	−.70	−.00	.26	.60
12	−6.79	.03	.04	−.02	−.05	.00	.00	.72	.01	.00	−.23	.00	−.00
13	−5.19	.01	−.02	−.01	−.24	−.00	.00	.58	.01	−.00	−.06	.00	−.00
14		−.01	.08	.04	.24	.00	.00	−.10	−.00	.00	.22	−.00	.00
15		−.00	−.00	.00	.00	.02	.05	−.00	.05	.01	−.00	.03	−.01
16		−.00	−.00	.00	−.00	.05	−.02	.00	−.01	.05	−.00	.01	.03
17		−.00	−.00	−.00	.00	.01	−.06	−.00	−.00	−.00	.00	−.01	−.03
18		.00	−.00	−.00	−.00	.06	.01	.00	−.00	.00	−.00	−.03	.01
19		−.00	.00	−.00	−.00	.02	.12	−.00	.05	.08	.00	.01	−.01
20		−.00	.00	−.00	−.00	.12	−.02	.00	−.08	.05	.00	.01	.01
21		−.04	−.02	−.01	.12	.00	−.00	−.07	−.00	−.00	−.07	.00	−.00
22		−.01	−.01	−.01	−.03	−.00	−.00	.04	.00	−.00	−.01	.00	.00
23		−.01	−.06	−.01	−.08	−.00	−.00	.00	.00	−.00	−.04	.00	.00

No.		⟨13⟩	⟨14⟩	⟨15⟩	⟨16⟩	⟨17⟩	⟨18⟩	⟨19⟩	⟨20⟩	⟨21⟩	⟨22⟩	⟨23
	ε_i	−3.36										
		$5\sigma(B)$	$3E(A)$	$3E'(A)$	$8A_1(A)$	$4E(A)$	$4E'(A)$	$9A_1(A)$	$10A_1(A)$	$2\pi(B)$	$2\pi'(B)$	$6\sigma(B)$
1	−31.77	−.04	.00	.00	−.02	−.00	.00	−.00	.00	.00	−.00	−.01
2	−30.96	.01	.00	.00	−.01	−.00	−.00	.03	.01	−.00	.00	.00
3	−25.54	−.10	−.00	−.00	.06	.00	−.00	.01	−.04	−.00	.00	−.04
4	−14.32	−.14	−.00	.00	.01	−.00	−.00	−.15	−.01	−.00	.00	−.03
5	−10.66	−.00	.06	.04	.00	−.04	.12	.00	−.00	−.04	−.02	.00
6	−10.66	.00	.04	−.06	−.00	−.12	−.04	−.00	.00	.02	−.04	−.00
7	−10.38	.11	.00	.00	−.24	−.00	.00	−.07	.09	−.00	−.00	.02
8	−7.57	.00	.06	−.01	.00	−.04	−.01	.00	−.00	.03	.00	−.00
9	−7.57	.00	.01	.06	−.00	−.01	.04	−.00	.00	.00	−.03	−.00
10	−7.07	−.00	−.02	.04	.00	−.00	.06	.00	−.00	.01	.00	−.00
11	−7.07	.00	.04	.02	.00	−.06	−.00	.00	−.00	−.00	.01	.00
12	−6.79	.64	−.00	−.00	−.01	.00	.00	.10	−.02	.00	−.00	.04
13	−5.19	−.63	.00	.00	−.34	−.00	.00	−.09	.07	−.00	.00	−.01
14		.26	.01	.00	−.83	.00	.00	−.24	.14	−.00	−.00	−.18
15		−.00	.68	−.26	.00	−.00	.04	.00	−.00	.64	.26	.00
16		−.00	.26	.68	.00	.04	.00	.00	−.00	.26	−.64	.00
17		.00	.12	.65	.00	.04	−.23	.00	−.00	−.13	.69	−.00
18		−.00	.65	−.12	.01	.23	.04	.00	−.00	−.69	−.13	.00
19		.00	.16	−.01	.00	−.93	−.25	.00	−.00	−.15	−.06	−.00
20		.00	.01	.16	.00	−.25	.93	.00	.00	−.06	.15	−.00
21		−.08	.00	−.00	−.23	−.00	.00	.93	.11	−.00	−.00	.10
22		.01	−.00	.00	.23	.00	.00	.07	.67	−.00	−.00	−.70
23		−.03	.00	.00	−.06	.00	.00	.15	−.71	−.00	−.00	−.63

CH_3-CH

No.		⟨1⟩	⟨2⟩	⟨3⟩	⟨4⟩	⟨5⟩	⟨6⟩	⟨7⟩	⟨8⟩	⟨9⟩	⟨10⟩	⟨11⟩	⟨12
	ε_i	−34.41	−22.32	−14.90	−14.51	−13.54	−8.72						
		$1A$	$2A$	$3A$	$4A$	$5A$	$6A$	$7A$	$8A$	$9A$	$10A$	$11A$	$12A$
1	−35.79	1.00	.05	.04	.04	.02	−.01	−.01	−.01	−.02	.00	.01	−.01
2	−21.77	−.06	.95	.05	.23	−.01	−.01	.05	−.04	−.16	.06	.00	−.02
3	−15.85	.05	.14	−.93	−.26	−.11	−.00	.03	.02	.13	−.04	−.02	.08
4	−14.35	−.02	−.09	−.24	.39	.88	.02	−.01	−.03	−.08	.00	.03	−.03
5	−12.81	−.01	−.17	−.22	.79	−.42	−.12	−.30	−.00	.03	.09	.04	−.10
6	−8.29	.01	.02	.01	.10	−.06	.97	−.07	−.07	.17	−.03	.05	.06
7		−.01	−.02	−.06	−.25	.01	.09	−.66	−.17	−.65	−.01	.09	−.15
8		.01	−.18	−.13	.11	−.17	.14	.67	−.11	−.63	.05	.10	−.13
9		.00	.01	−.01	.01	.00	.08	−.05	.97	−.20	.00	.10	.09
10		.00	−.01	.02	.14	−.04	−.00	−.01	−.03	−.20	−.70	−.50	.45
11		−.01	.04	.02	.02	−.02	−.09	.03	−.05	.09	−.59	.79	−.02
12		.00	−.03	.01	.02	−.01	−.06	−.03	−.13	−.11	.38	.30	.85

The opposite frontier interaction is found in the second highest, occupied MO of the transition state; it is mainly composed from the π-bonding HOMO and the C_3—C_4 σ-antibonding, unoccupied MO 13 of the educt. Thus, while the transformation matrix agrees with the expectations concerning the most important orbitals in this reaction, it reveals that contributions from subjacent MO's like MO 8 and MO 17 are not negligible in the transition state.

3.2. *Addition of singlet methylene to ethylene*

Previous calculations of reaction (2) on *ab initio* [15] as well as semiempirical [16] level focussed their attention mainly upon the geometry and energetic of the reaction course.

$$CH_2 + C_2H_4 \longrightarrow \triangle \qquad (2)$$

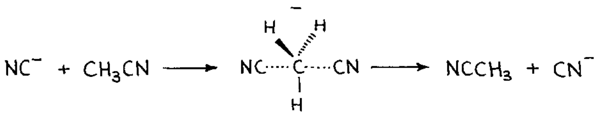
Our calculated activation barrier of 5.9 kcal/mol agrees with previous MNDO calculations [16b] while *ab initio* [15] as well as MINDO/2 [16a] results indicate that reaction (2) should have no barrier. As MNDO is known to disfavour bridged structures [17], the calculated barrier has no physical meaning.

However, the geometry of the calculated transition structure is in accord with the calculated mode of approach by *ab initio* methods [15], showing an "inward" bending of the methylene group. A non-linear approach is also predicted by the symmetry of the frontier orbitals [18].

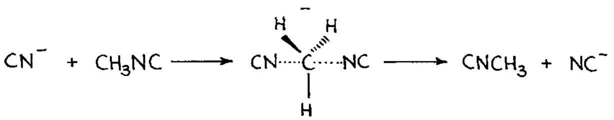
The transformation matrix shows that the only significant orbital interaction occurs among the two HOMOs and the two LUMOs. In fact, there is very little electronic redistribution in the transition state at all pointing to a low activation barrier.

3.3. Nucleophilic substitution of CH_3CN *and* CH_3NC *by* CN^-

It has been shown that also substitution reactions can be understood in terms of the most important interacting orbitals [19]. Perturbational treatment leads to the familiar concept of hard and soft acids and bases [4, 20]. The reaction course involving a nucleophile owing a high lying HOMO should be governed by this orbital, whereas nucleophiles with a large, localized charge should be more directed by the coulomb attraction. This can be demonstrated with an ambident nucleophile like CN^-. While the σ-type lone-pair HOMO is more located on carbon, the negative charge is mainly concentrated on nitrogen. The chemical consequences of this situation are known: Depending on the electrophile and the reaction condition, nitriles or isonitriles are the reaction products [21]. Here we investigate the degenerate substitutions of CH_3CN and CH_3NC by CN^-:



$$NC^- + CH_3CN \longrightarrow [NC\cdots CH_3\cdots CN]^- \longrightarrow NCCH_3 + CN^- \qquad (3)$$



$$CN^- + CH_3NC \longrightarrow [CN\cdots CH_3\cdots NC]^- \longrightarrow CNCH_3 + NC^- \qquad (4)$$

The values in Tables 2c and 2d show that the transition state for reaction (3) has a shorter bond length for the C—CN bonds than for C—NC in reaction (4). This agrees with an orbital controlled reaction having better orbital interaction and therefore larger overlap and shorter bond lengths in the transition state. Reaction (3) also needs less activation energy than reaction (4).

Table 3c shows that for the nitrile substitution (3) the most important interaction occurs between the HOMO of CN^- (denoted B) and the unoccupied MO $8A_1$

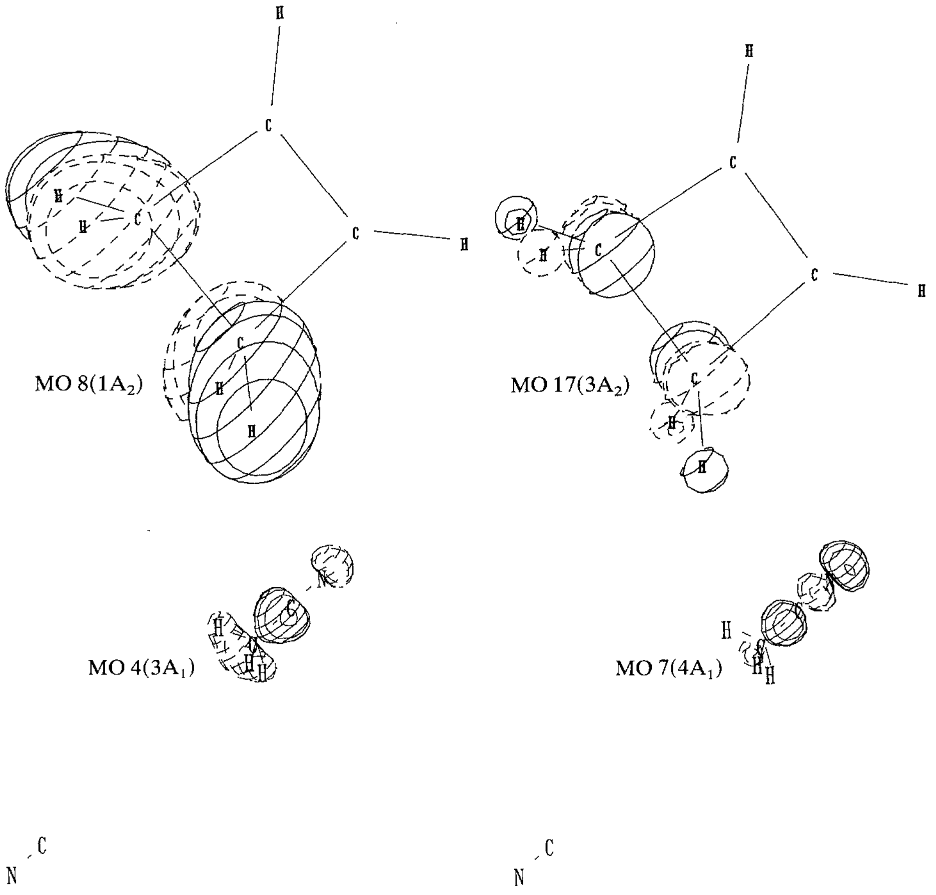


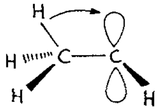
Fig. 1. Contour maps of MO's 8 and 17 of cyclobutene and MO's 4 and 7 of acetonitrile. The lines correspond to an electron density of 0.01 a.u. [28]

of CH_3CN (denoted A), which is C—C σ-antibonding. The two occupied MO's 4 and 7 describe the leaving CN^- group in the HOMO of the transition state and correspond to MO 13 since the two nitrile groups are undistinguishable.

The transformation matrix for the isonitrile reaction (4) in Table 3d reveals characteristic differences. Again, the most important interaction takes place between the occupied MO's of the nitrile groups, $6A_1(A)$, $7A_1(A)$ and $5\sigma(B)$, and the unoccupied $8A_1(A)$. However, the coefficient of the unoccupied MO is smaller compared to reaction (3), which is expected for a reaction which has less favoured orbital interaction. Furthermore, the unoccupied MO 16 now interacts also with the much lower-lying, σ-bonding MO's of the nitrile groups represented by the MO's 4 and 7 of A and MO 10 of B. As the lone-pair HOMO of CN^- is located more on carbon and therefore on the backside of the attacking nucleophile, the σ-bonding MO 10 becomes more liable for interaction in spite of its lower energy level as it is the next highest with σ-symmetry.

3.4. *Rearrangement of methylcarbene to ethylene*

In previous investigations it was concluded that the mechanism of carbene rearrangement towards olefines in the singlet states is characterized by moving of the C—R bonding towards the empty *p*-orbital of the divalent carbon [22]:



$$\longrightarrow C_2H_4. \qquad (5)$$

The alteration in the electronic structure methylcarbene along the reaction coordinate was determined by plotting the electron density maps of the MO's of educt, transition state and product [23]. Following the shapes of the MO's it was shown that the relevant C—H bonding MO, being the third highest in the carbene, becomes the second highest in the transition state and finally the C—C π-bonding HOMO in ethylene. A systematic investigation of 1,2 rearrangements of carbenes, carbonylcarbenes, nitrenes and carbonylnitrenes using transformation matrices agrees with this picture but shows that in some cases other orbitals have to be considered [24].

The geometries of educt and transition state of reaction (5) are shown in Table 2e.

In agreement with the Hammond postulate [25], the transition-state structure is more carbene-like. Again, the activation barrier is calculated too high in comparison with *ab initio* calculations including CI [26]. The transformation matrix in Table 3e shows that the C—H* bonding MO 4 (H* being the migrating hydrogen) of the educt becomes MO 5 of the transition state with some mixing of MO 5 of the carbene and, more important, with a contribution of 0.30 by the LUMO. Thus, the qualitative picture of Yates et al. [23] has been supported in our quantitative investigation showing the contribution of the LUMO.

4. Conclusion

The calculation of the transformation matrix between educt and transition state is a simple, but very effective way to gain insight into the orbital mixing and orbital interaction of reacting molecules. The most important orbitals of the educts to explain a reaction mechanism which can otherwise only be supposed by their symmetry and energy levels can exactly be deduced and their contribution to the transition state may be determined. This was demonstrated for four different reaction mechanisms. Our results are in agreement with previous investigations which are mostly focussed on the educts, but they provide a quantitative measure for the orbital interaction and they show that in some cases orbitals are important which have not been thought of from FMO consideration. Transformation matrices may become a valuable tool especially in cases where the most important interacting orbitals are not directly obvious. They offer a link between the electronic structure of educt and transition state which are the most important points on the potential energy hyperface.

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References

1. Fukui, K., Fujimoto, H.: Bull. Chem. Soc. Japan **41**, 1989 (1968)
2. Fukui, K., Fujimoto, H.: Bull. Chem. Soc. Japan **42**, 3399 (1969)
3. Fukui, K.: Theory of orientation and stereoselection. Berlin: Springer-Verlag, 1975
4. Fleming, I.: Frontier orbitals and organic chemical reactions. New York: Wiley, 1976
5. Berson, J. A., Salem, L.: J. Am. Chem. Soc. **94**, 8917 (1972)
6. Epiotis, N. D.: Theory of organic reactions. Berlin: Springer-Verlag, 1978
7. Frenking, G.: J. Mol. Struct. THEOCHEM **104**, 233 (1983)
8. Dewar, M. J. S., Thiel, W.: J. Am. Chem. Soc. **99**, 4899 (1977)
9. a) McIver, Jr., J. W., Komornicki, A.: Chem. Phys. Letters **10**, 303 (1971); b) Poppinger, D.: Chem. Phys. Letters **35**, 550 (1975)
10. Dewar, M. J. S., Kirschner, S.: J. Am. Chem. Soc. **93**, 4290 (1971)
11. McIver, Jr., J. W., Komornicki, A.: J. Am. Chem. Soc. **94**, 2625 (1972)
12. Stephenson, L. M., Brauman, J. I.: Acc. Chem. Res. **7**, 65 (1974)
13. Dewar, M. J. S., Haselbach, E.: J. Am. Chem. Soc. **92**, 590 (1970)
14. Ref. 4, p. 103f.
15. a) Rondan, N., Houk, K. N., Moss, R. A.: J. Am. Chem. Soc. **102**, 1770 (1980); b) Zurawski, B., Kutzelnigg, W.: J. Am. Chem. Soc. **100**, 2654 (1978)
16. a) Bodor, N., Dewar, M. J. S., Wasson, J. S.: J. Am. Chem. Soc. **94**, 9095 (1972); b) Schoeller, W. W., Aktekin, N.: J. Chem. Soc. Chem. Comm. 20 (1982)
17. Frenking, G., Schwarz, H.: Z. Naturforsch. **36b**, 797 (1981)
18. Ref. 4, p. 96.
19. Fujimoto, H., Yamabe, S., Fukui, K.: Tetrahedron Letters 439 (1971)
20. a) Salem, L.: J. Am. Chem. Soc. **90**, 543 (1968); b) Klopman, G.: J. Am. Chem. Soc. **90**, 223 (1968); c) Pearson, R. G.: J. Am. Chem. Soc. **85**, 3533 (1963); d) Pearson, R., Songstad, J.: J. Am. Chem. Soc. **89**, 1827 (1967)
21. Ref. 4, p. 40f
22. Jones, W. M.: Rearrangements in ground and excited states. P. deMayo (ed.), Vol. 1, Essay 3. New York: Academic Press, 1980
23. Altmann, J. A., Csizmadia, I. G., Yates, K.: J. Am. Chem. Soc. **97**, 5217 (1975)
24. Frenking, G., Schmidt, J.: Tetrahedron, in press
25. Hammond, G. S.: J. Am. Chem. Soc. **77**, 334 (1955)
26. Raghavachari, K., Frisch, M. J., Pople, J. A., Schleyer, P. v. R.: Chem. Phys. Letters **85**, 145 (1982)
27. Keller, E.: Chem. unserer Zeit **14**, 56 (1980)
28. Jorgensen, W. L., Salem, L.: Orbitale organischer Moleküle. Weinheim: Verlag Chemie, 1974

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