

AB INITIO CALCULATIONS AND ASSIGNMENT OF PHOTOELECTRON SPECTRA OF MALEIC AND SUCCINIC ANHYDRIDE¹

M. ALMEMARK, J. E. BÄCKVALL, C. MOBERG and B. ÅKERMARK*
 Department of Organic Chemistry

L. ÅSBRINK

Physics Department, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden

and

B. ROOS

Institute of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden

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Abstract—The results from *ab initio* calculations on maleic and succinic anhydride are presented. A good correlation is obtained between the calculated orbital energies and the ionization potentials obtained from the photoelectron spectra of the molecules. The photochemistry of cyclohexadiene is discussed on the basis of the concepts of through bond and through space interaction.

Recent photochemical studies of simple 1,4-cyclohexadiene systems show that they behave quite differently to 1,4-bridged systems (1). While the 1,4-bridged systems (1) generally give tetracyclic products (2) derived from cycloaddition,^{2,3} the open systems e.g. 3 give dimers,^{4,5} e.g. 4 and a rearranged product 5.⁷ This difference in the photochemistry of the two systems may be explained qualitatively by the use of the concepts of through bond and through space interaction.⁸ In a bridged cyclohexadiene like 1, the π -systems of the two "isolated" double bonds are in general sufficiently

close to permit interaction through space. In this way two ground state and two excited state π -orbitals are formed with the symmetries SS, SA and AS, AA relative to the two mirror planes depicted in Fig 2. The level ordering will be SS, SA for the

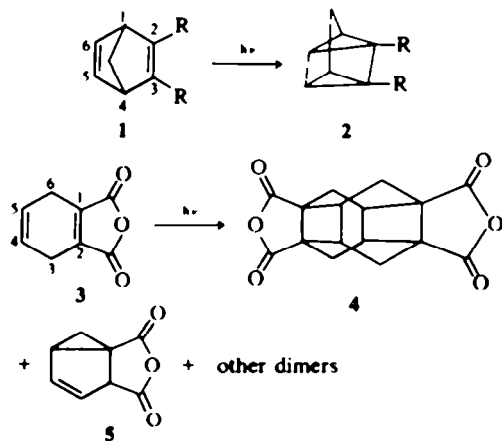


Fig 1.

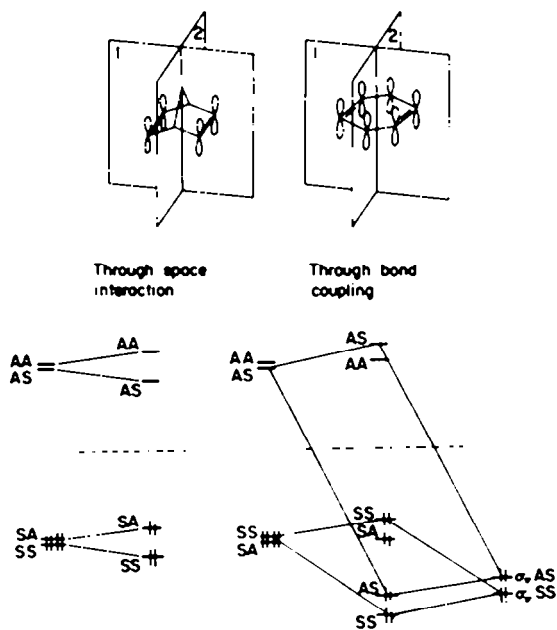


Fig 2.

ground state and AS, AA for the excited state orbitals. This type of ordering is most probably found among norbornadiene derivatives.⁸ The SS level for the parent molecule has been found to be 0.85 eV below the SA level.⁹ Evidence for the ordering AS, AA of the excited levels is found in the photochemical formation of quadricyclane derivatives (2), which should occur only when the excited orbital has AS symmetry and is bonding across the ring (2-6 and 3-5 in 1). The through space interaction in an unbridged cyclohexadiene, *e.g.* 3 which is essentially planar as determined by X-ray crystallography,¹⁰ should be smaller than in norbornadiene. In addition, two of the four σ -orbitals of the methylene groups have the correct symmetry for interaction with the π -system. If this interaction is sufficiently strong, it will lead to a reversal of the π -level ordering, that is the SA level falls below the SS level and the AA level below the AS level⁸ (Fig 2). Indirect evidence for the correctness of these conclusions is derived from the fact that the π -orbital splitting as determined by photoelectron spectroscopy is larger (1.0 eV) for cyclohexadiene than for norbornadiene (0.85 eV)⁹ where stronger through space interaction would be expected. Again, the anticipated level ordering in the excited state is in accordance with the photochemistry of the molecules involved. Despite numerous attempts, compounds analogous to the quadricyclanes have not been observed in the photolysis of open 1,4-cyclohexadienes. This is the result expected if the AA level falls below the AS level, since the first excited state will then be antibonding across the ring (1-5 and 2-4 in 3). Similar concepts have recently been used by Schmidt and Wilkins^{11a} to explain the failure of "hypostrophene" to undergo intramolecular photo cycloaddition and by Ahlgren^{11b} in calculations on substituted cyclohexadiene systems. In hypostrophene the central carbon-carbon σ -bond, which has than unusually high energy, can interact with the π -system.

In an attempt to determine quantitatively the magnitude of the interactions in the cyclohexadiene system 3 we have initiated a study of this system. We report here photoelectron spectra and *ab initio* calculations on two model compounds, maleic anhydride (6) and succinic anhydride (7) (Fig 3).

The calculated orbital energies of maleic anhydride and succinic anhydride are compared with the ionization energies from photoelectron spectra. The basis set used in the calculation was obtained from seven s-type and three p-type primitive Gaus-

sian functions for the C and O atoms.¹² This set was contracted to four s-type and two p-type orbitals. The basis set for hydrogen was formed from four s-type functions contracted to two.¹¹

In the calculation on maleic anhydride the experimental equilibrium geometry was used.¹⁴ The experimental geometry for succinic anhydride¹⁵ was modified to a planar ring system. Both molecules then belong to point group C_{2v} . The calculations were performed with the computer programme MOLECULE.¹⁶ The numbering of the atoms is shown in Fig 3.

RESULTS AND DISCUSSION

Total energies for maleic anhydride and succinic anhydride are calculated to be -376.656 and -377.837 a.u., respectively. Valence orbital energies and populations are given in Tables 1 and 2.

Table 1. Orbital energies in maleic anhydride (I) and in succinic anhydride (II) (in eV)

Orbital	I	II
<i>Core orbitals</i>		
1a ₁ (O ₁)	562.96	562.71
1b ₂ (O ₂)	561.64	560.93
2a ₁ (O ₃)	561.63	560.93
2b ₂ (C ₁)	311.63	311.26
3a ₁ (C ₁)	311.63	311.26
4a ₁ (C ₂)	308.66	307.88
3b ₂ (C ₂)	308.62	307.87
<i>Valence orbitals</i>		
5a ₁	42.030	42.203
4b ₂	40.259	39.782
6a ₁	38.846	38.364
7a ₁	32.009	31.641
5b ₂	26.257	27.255
6b ₂	23.205	23.960
8a ₁	22.682	22.258
9a ₁	19.900	19.100
1b ₂ (π)	19.035	20.104
7b ₂	18.571	18.483
10a ₁	18.177	16.884
8b ₂	17.324	17.047
11a ₁	16.624	15.612
1a ₂ (π)	15.764	16.656
2b ₂ (π)	13.633	17.367
12a ₁	13.585	13.156
9b ₂	12.694	12.199
3b ₁ (π)	12.077	12.749
2a ₂ (π)		14.023

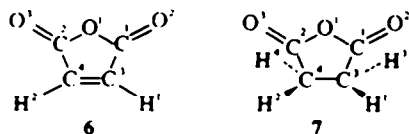


Fig 3. Numbering of the atoms in maleic anhydride and succinic anhydride.

The assignment of photoelectron spectra by means of orbital energies is not straight forward. As is well known, reorganization and correlation effects will affect the ionization potentials. The order of the ionization potentials might therefore be different from the order of the orbital energies. In a recent paper Roos *et al.*¹⁷ were able to make assign-

Table 2a. Outer valence orbitals for maleic anhydride

	Gross atomic population					Bonding character				
	C ₁	C ₂	O ₁	O ₂	H ₁	C ₁ -O ₁	C ₁ -O ₂	C ₁ -C ₂	C ₂ -C ₄	C ₂ -H ₁
<i>σ</i> -sym										
5b ₂	0.43	0.29	0.23	0.12	0.04	wb	nb	sb	nb	wb
6b ₂	0.27	0.21	0.65	0.12	0.07	b	wb	nb	wab	wb
8a ₁	0.26	0.45	0.31	0.06	0.07	nb	nb	nb	sb	wb
9a ₁	0.11	0.35	0.07	0.42	0.09	nb	nb	nb	wb	b
7b ₂	0.16	0.14	0.12	0.54	0.10	nb	wb	wab	wab	b
10a ₁	0.14	0.32	0.02	0.45	0.08	nb	wb	nb	b	wb
8b ₂	0.21	0.29	0.01	0.34	0.14	nb	wb	b	ab	b
11a ₁	0.11	0.11	1.03	0.21	0.05	nb	wb	nb	wb	wb
12a ₁	0.04	0.21	0.34	0.58	0.00	wab	wb	nb	wb	nb
9b ₂	0.02	0.13	0.28	0.68	0.02	nb	wb	wab	sab	nb
<i>π</i> -sym										
1b ₁	0.36	0.07	0.85	0.15	—	b	b	wb	nb	—
1a ₂	0.34	0.01	—	0.60	—	—	sb	nb	nb	—
2b ₁	0.04	0.23	0.94	0.26	—	wab	wb	wb	b	—
3b ₁	0.01	0.65	0.02	0.33	—	nb	wb	wab	sb	—

Table 2b. Outer valence orbitals for succinic anhydride

	Gross atomic population					Bonding character				
	C ₁	C ₂	O ₁	O ₂	H ₁	C ₁ -O ₁	C ₁ -O ₂	C ₁ -C ₂	C ₁ -C ₄	C ₂ -H ₁
<i>σ</i> -sym										
5b ₂	0.34	0.44	0.12	0.08	0.04	wb	nb	sb	ab	wb
6b ₂	0.26	0.16	0.80	0.13	0.03	sb	nb	ab	ab	wb
8a ₁	0.28	0.38	0.38	0.05	0.05	nb	wb	wa	b	wb
9a ₁	0.15	0.14	0.15	0.61	0.01	nb	nb	nb	wb	nb
7b ₂	0.21	0.19	0.12	0.43	0.06	nb	b	wab	ab	b
10a ₁	0.16	0.31	0.19	0.41	0.01	wab	b	wb	b	nb
8b ₂	0.25	0.19	0.02	0.47	0.04	nb	wb	wb	wab	wb
11a ₁	0.04	0.37	0.88	0.03	0.06	wb	nb	wab	sb	wb
12a ₁	0.05	0.23	0.20	0.62	0.00	ab	wb	nb	wb	nb
9b ₂	0.03	0.12	0.26	0.70	0.01	nb	wb	wab	sab	wab
<i>π</i> -sym										
1b ₁	0.21	0.39	0.35	0.06	0.08	wb	wb	wb	b	b
2b ₁	0.12	0.26	0.75	0.07	0.08	b	wb	wab	b	b
1a ₂	0.24	0.32	—	0.23	0.11	—	b	b	ab	b
2a ₂	0.14	0.24	—	0.41	0.10	—	b	ab	ab	b
3b ₁	0.07	0.01	0.67	0.59	0.00	ab	b	nb	nb	nb

ments of the photoelectron spectra for benzene and the azabenzenes by means of an empirical correction added to the orbital energies. It was assumed that the reorganization and correlation corrections should be very similar for orbitals of similar structure. This is equivalent to the assumption that the variation of an orbital energy along a series of similar molecules reflects the variation of the corresponding ionization potential. This was indeed found to be the case for the azabenzenes and it was possible to make a full assignment of all peaks in the spectra. The empirical corrections were found from a comparison with experimental ionization potentials in cases where the assignments were unam-

biguous. The ionization potentials estimated in this way differed in almost all cases less than 0.5 eV from the experimental values. The somewhat larger differences found in a few cases all referred to broad or poorly resolved bands. The empirical corrections were found to vary smoothly with the orbital energies: from -5.7 to -1.4 eV for the *σ*-orbitals with the larger corrections for the inner orbitals and from -1.8 to 0.0 eV for the *π*-orbitals.

The present *ab initio* calculations on the two similar molecules maleic anhydride and succinic anhydride were made with the same basis set as was used for the azabenzenes. It is therefore tempting to investigate whether the same corrections can

be used for the assignments of the photoelectron spectra in these molecules. That the assignment obtained in this way is correct could then be checked by a study of the true empirical corrections. They should be nearly equal for orbitals of similar structure and should vary in the same smooth way with energy as for the azabenzenes.

The 304 Å photoelectron spectra of the two molecules are shown in Figs 4 and 5 together with ionization potentials estimated by means of the azabenzene corrections. These ionization potentials agree well with the peaks in the spectra and it is therefore possible to use them for an assignment

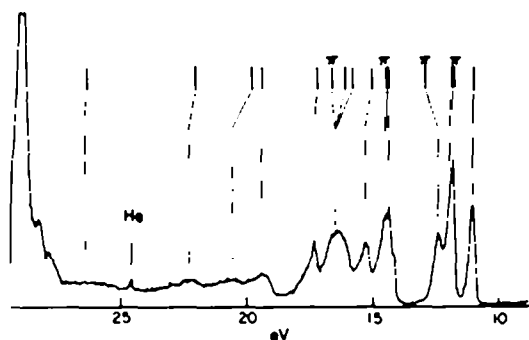


Fig. 4. Photoelectron spectra of maleic anhydride.

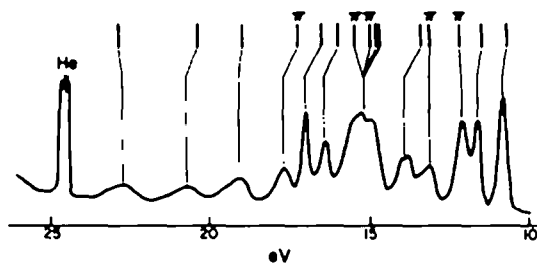


Fig. 5. Photoelectron spectra of succinic anhydride.

of the various peaks. The result is presented in Table 3 which gives the orbital energies, ionization potentials, and the corresponding empirical corrections.

A good test on the reliability of the assignment can be obtained by a comparison of similar orbitals in the two molecules. It can be expected that reorganization and correlation corrections should be nearly equal for orbitals of similar structure. The similarity in structure can be checked from the population analyses data given in Tables 2a and 2b. Thus, we ought to obtain the same empirical corrections for corresponding orbitals. As can be seen from Table 3 this is also the case to within 0.5 eV for all σ -orbitals, except $6b_2$. The exact location of the vertical ionization potentials is, however, difficult to determine for this diffuse band. The situation is

Table 3. Orbital energies and ionization potentials for maleic anhydride (I) and succinic anhydride (II) (in eV)

Orbital	I			II		
	-E	IP	diff.	-E	IP	diff.
σ -orbitals						
5a ₁	42.0	—	—	42.2	—	—
4b ₂	40.3	—	—	39.8	—	—
6a ₁	38.8	—	—	38.4	—	—
7a ₁	32.0	26.3	-5.7	31.6	—	—
5b ₂	26.3	22.3	-4.0	27.3	22.9	-4.4
6b ₂	23.2	20.4	-2.8	24.0	20.6	-3.4
8a ₁	22.7	19.4	-3.3	22.3	19.0	-3.3
9a ₁	19.9	17.4	-2.5	19.1	17.0	-2.1
7b ₂	18.6	~16.5	~2.1	18.5	16.4	-2.1
10a ₁	18.2	~16.5	~1.7	16.9	~15.3	~1.6
8b ₂	17.3	15.3	-2.0	17.0	~15.3	~1.7
11a ₁	16.6	14.5	-2.1	15.6	13.8	-1.8
12a ₁	13.6	12.0	-1.6	13.2	11.6	-1.6
9b ₂	12.7	11.1	-1.6	12.2	10.8	-1.4
π -orbitals*						
1b ₁	19.0	16.5	-2.5	20.1	17.7	-2.4
1a ₂	—	—	—	16.7	15.3	-1.4
2b ₁	—	—	—	17.4	15.3	-2.1
1a ₂ /2a ₂	15.8	14.5	-1.3	14.0	13.1	-0.9
2b ₁ /3b ₁	13.6	12.5	-1.1	12.7	12.1	-0.6
3b ₁	12.1	12.0	-0.1	—	—	—

* Orbitals antisymmetric with respect to reflection in the plane of the heavy atoms.

somewhat more complicated for the π -orbitals. Only in maleic anhydride are these orbitals of the ordinary π -type. The correction to the orbital energies is in this case very similar to the π -orbital corrections found for the azabenzene, ranging from around -2 eV for the innermost orbital to around zero for the outermost one. In succinic anhydride these orbitals are mixed with the C-H bonding orbitals and are thus not of pure π -type. The corrections in this case lie between the values for σ - and π -orbitals. The corrections shown in Table 3 are very similar to those obtained for the azabenzene. As expected they are larger for the inner orbitals and vary in a smooth way with the orbital energies. There is one interesting exception to this. The difference between ionization potentials and orbital energy is smaller than expected for the orbital 6b. This can be explained by the fact that this orbital has its main population at the ring oxygen and thus has very little 2s-character (*cf* Tables 1 and 2). This decreases the reorganization energy compared to the surrounding orbitals, which have larger 2s-character.

The result from a population analysis using Mulliken's method is shown in Table 4. In both molecules the charge on C₁, which has two oxygens as neighbours, is $+0.75$. The ring oxygen has a

value of -0.67 . This can be compared with the oxygen in furan where q (O) is -0.41 .¹⁸ The high electron density on the ring oxygens (and outer oxygens) in maleic and succinic anhydride is in accordance with the known basicity of anhydrides.¹⁹ The charges on C₁ (-0.50) and H₁ ($+0.27$) in succinic anhydride indicates that the C-H bond should be rather polarized. The dipole moments for maleic and succinic anhydride are experimentally 3.94 D²⁰ and 4.20 D.²¹ This *ab initio* calculation gives 5.11 D and 5.80 D, respectively.

The results obtained on model systems in this and previous work⁹ indicate that the situation in the compound 3 is quite complex. The ionization potential for the highest π -orbital of maleic anhydride is 12.0 eV while that obtained for normal olefins is considerably smaller, e.g. for ethene 10.5 eV²² and for cyclohexene 9.12 eV.⁹ Considering this large difference in energy, it is difficult even to make a qualitative estimate of the through space interaction between the double bonds in cyclohexadiene 3, but it should be relatively small. By contrast, the interaction between at least the double bond of the maleic anhydride type and the methylene σ -orbitals of π -symmetry of 3 should be strong since the energy difference between the systems is decreased compared to the unsubstituted cyclohexadiene. A study of the compound 3, using the results obtained here, is obviously of some interest and is under way.

Table 4. Gross atomic population and charges for maleic and succinic anhydride

	Maleic anhydride	Succinic anhydride
C ₁ (s-orb)	2.97	2.96
C ₁ (p σ -orb)	1.48	1.50
C ₁ (p π -orb)	0.79	0.78
C ₁ (tot pop)	5.25	5.24
q (C ₁)	+0.75	+0.76
C ₂ (s)	3.19	3.38
C ₂ (p σ)	2.09	1.90
C ₂ (p π)	0.96	1.22
C ₂ (tot pop)	6.25	6.50
q (C ₂)	-0.25	-0.50
O ₁ (s)	3.92	3.90
O ₁ (p σ)	2.95	3.00
O ₁ (p π)	1.81	1.77
O ₁ (tot pop)	8.67	8.67
q (O ₁)	-0.67	-0.67
O ₂ (s)	3.91	3.91
O ₂ (p σ)	3.20	3.20
O ₂ (p π)	1.34	1.36
O ₂ (tot pop)	8.46	8.47
q (O ₂)	-0.46	-0.47
H ₁ (s)	0.71	0.73
q (H ₁)	+0.29	+0.27

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