229. Photoelectron Spectra of Vicinal Tricarbonyls

by **Peter Bischof, Rolf Gleiter** and **Peter Hofmann**

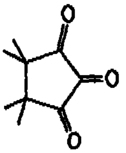
Institut für Organische Chemie der Technischen Hochschule Darmstadt and
Institut für Organische Chemie der Universität Erlangen

(30. V. 75)

Summary. The He I photoelectron spectra of tetramethylcyclopentane-1,2,3-trione **1**, 4,4,6,6-tetramethylcyclohexane-1,2,3-trione **2**, bicyclo[1.2.3]octane-2,3,4-trione **3**, bicyclo[2.2.3]nonane-2,3,4-trione **4** and anhydrous ninhydrine **5** are presented. The assignment of the first two bands is discussed using semiempirical calculations together with a qualitative band shape analysis. It is shown that the first two bands in **1** to **4** are due to the ionization of an electron from lone pair combinations of the 2*p*-oxygen orbitals.

While the electronic structure and the different states of α-diketones have aroused growing interest in the last ten years[1] [1], investigations of the electronic properties of tricarbonyls are sparse and mostly only qualitative basis [2] [3]. The PE. spectrum of pentane-2,3,4-trione has been reported [4] and, based on MINDO/2 calculations, a helical arrangement of the carbonyl groups was assumed with a dihedral angle of 90°. However, recent X-ray analysis [5] shows that the dihedral angle in pentane-2,3,4-trione is 120°.

By extension of our interest in the electronic structure of α-diketones [6] we have investigated the photoelectron (PE.) spectra of several cyclic vicinal triketones in which, for steric reasons, the dihedral angles between the carbonyl groups are confined to a narrow range, which can be estimated accurately from *Dreiding* models. In this communication we report the PE. spectra of tetramethylcyclopentane-1,2,3-trione (**1**) [2], 4,4,6,6-tetramethylcyclohexane-1,2,3-trione (**2**) [7], bicyclo[3.2.1]octane-2,3,4-trione (**3**) [8], bicyclo[3.2.2]nonane-2,3,4-trione (**4**) [8], and anhydrous ninhydrin (**5**).



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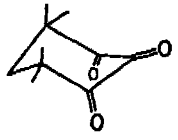
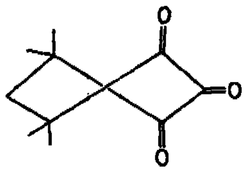


2a



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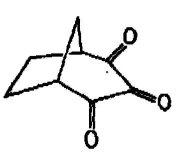

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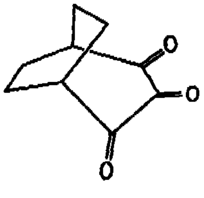

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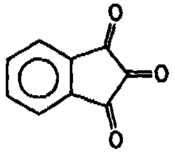

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[1] For more important references see [1].

For **5**, an X-ray structure analysis has been reported [9]; as anticipated the molecule was found to be planar. From *Dreiding* models only one conformation seems likely for **1**, **3** and **4**. For **1** a planar molecule is anticipated; for **3** (C_s) the dihedral angle between the central CO-group and those adjacent is estimated to be ≈ 25°; for **4** there are two OCCO dihedral angles, estimated to be 40° and 70° respectively. In the case of **2** two conformations **2a** (C_s) and **2b** (C_2) should have a similar energy. In **2a** the six-membered ring exists in a rigid chair-conformation in which case the dihedral angle between the central CO group and those adjacent is estimated to be ≈ 50° [10]. In **2b** the six-membered ring has a flexible twist conformation, estimated to have a 5.5 kcal/mol higher energy than the chair form for cyclohexane [11]. In **2b**, however, the interaction between the methyl groups has vanished resulting in a gain of 5.4 kcal/mol compared with **2a**, and the dihedral angle between the carbonyl groups is estimated to be ≈ 30° [11].

The PE. spectra of **1**, **3** and **5** are shown in Fig. 1[2]. The first bands of **1** to **5** are correlated in Fig. 2.

At first sight it seems surprising that the first bands possess quite a similar ionization potential although the O...O distances range from 2.6 Å to 3.1 Å due to the different geometries; it indicates qualitatively that through-bond interaction is most probably dominant.

Assuming *Koopmans'* theorem ($-\varepsilon_J = I_{v,J}$) [12] molecular orbital calculations[3] help to interpret the first bands of the PE. spectra. Semiempirical molecular orbital calculations of the extended *Hückel* (EHT) [13][4] and CNDO/2 [14] type predict that through-bond interaction [15] dominates between the p-lone pairs of the carbonyl groups [16]. This has been demonstrated for α-diketons [6] and for pentane-2,3,4-trione) [4] as a representative of an open chain trione.

In Fig. 3 the interaction between the semilocalized C–C σ-orbitals and the 2p-orbitals on the oxygen atoms is shown schematically for cyclopentane-1,2,3-trione. It is seen that through-bond interaction affects mainly the bonding b_2-lone pair combination yielding the sequence b_2, a_1, b_2.

Analogous to diazabicyclo[2.2.2]octane [17] and pyrazine [18] where through-bond interaction is dominant we expect, for the first band, a shape where a higher vibrational component $v' \leftarrow 0$ is the most intense of the progression *i.e.* the adiabatic ionization potential ($I_{a,J}$) is not equal to the vertical one ($I_{v,J}$). The band should have a smooth onset, due to the fact that ejection of an electron from b_2 weakens the C–C σ-bond. In contrast to this, for the band which corresponds to the a_1-orbital we expect a steep onset where the $0 \leftarrow 0$ vibrational component is the most intense of the progression *i.e.* $I_{a,J} = I_{v,J}$. This shape should be due to the fact that ionization occurs essentially from a nonbonding orbital.

From Fig. 1 we see that the first band of all the spectra has a relatively smooth onset while the second one exhibits a steep ascent. The possible deductions from these

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[2] The PE. spectra were measured on a PS 18 Photoelectron Spectrometer (*Perkin-Elmer* Ltd., Beaconsfield, England).

[3] For the molecular orbital calculations we assumed the following bond lengths: C–C = 1.50 Å, C–C = 1.40 Å, C–H = 1.10 Å, C=O = 1.22 Å. The spacial arrangement of the centers was taken from *Dreiding* models.

[4] The *Slater* exponent for hydrogen used was 1.3.

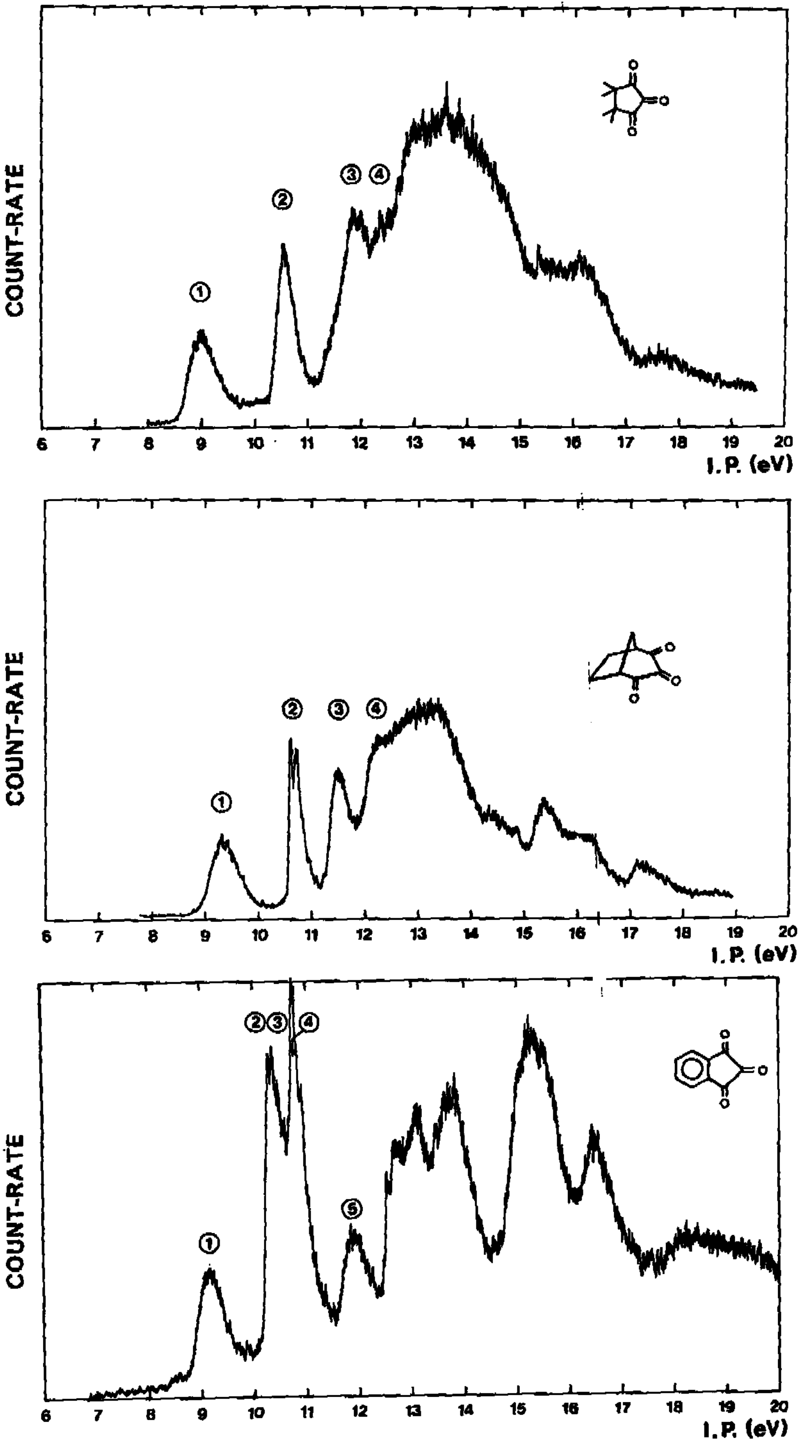


Fig. 1. *Photoelectron spectra of* **1**, **3** *and* **5**

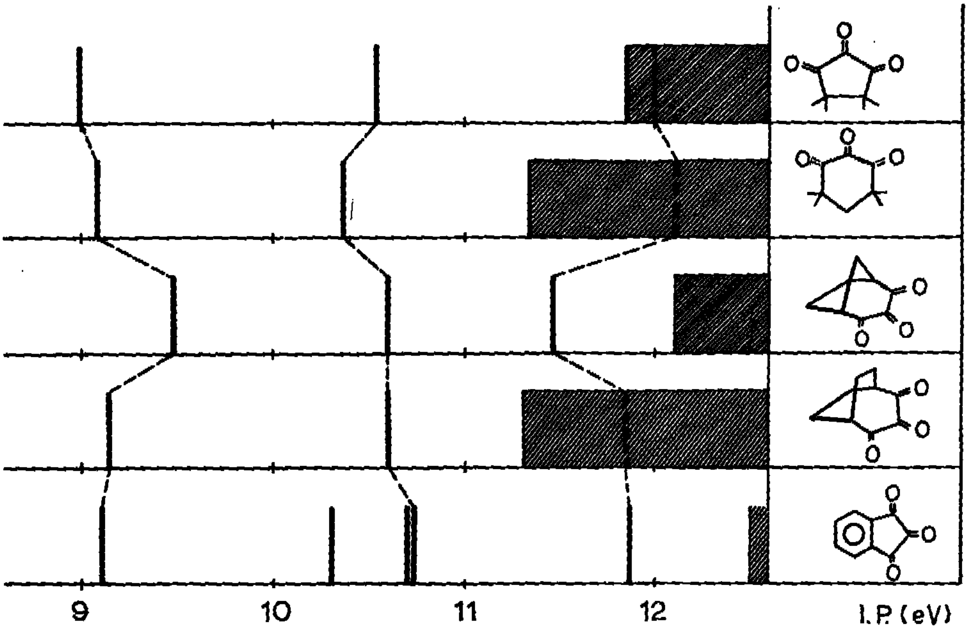


Fig. 2. *Correlation of the first bands of the PE. spectra of* **1** *to* **5**. *The dotted lines correlate the bands which are due to an ionization from a lone pair combination*

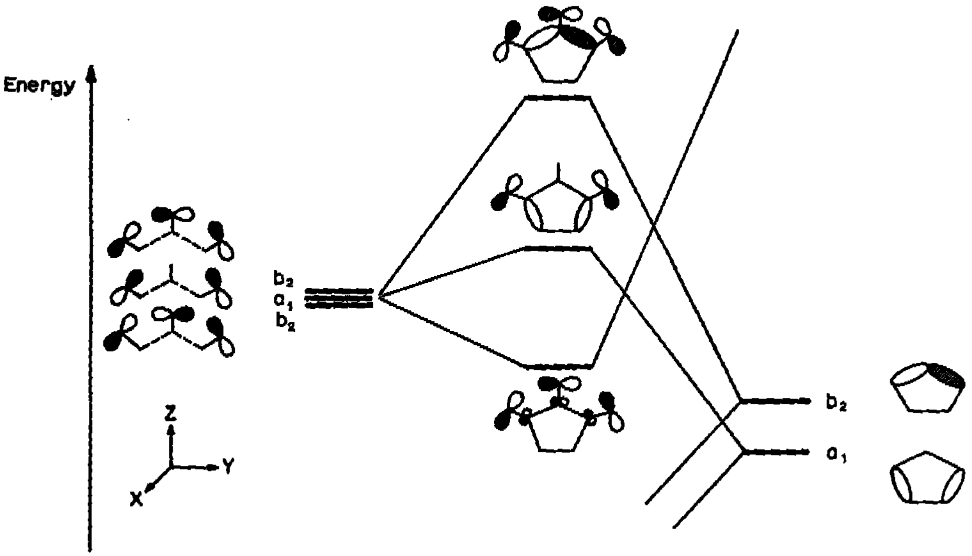
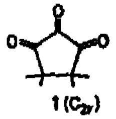
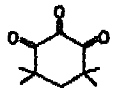
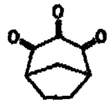
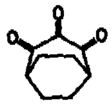
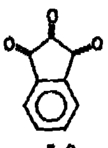


Fig. 3. *Qualitative interaction of the three lone pair combinations with the σ-orbitals of cyclopentane-1,2,3-trione*

facts are supported by semiempirical calculations which predict that the orbital energy of b_2 should be higher than that of a_1 by at least 0.6 eV (see Table, columns 4 and 5). A key compound for the assignment of the band corresponding to the second b_2 orbital is **5**. In its PE. spectrum we observe four peaks well separated from the region below 12 eV (see Fig. 1 and Table). From a comparison with the PE. spectra of **1–4** the assignment of band ① to the bonding b_2 combination is assured.

Semiempirical calculations of the EHT and CNDO/2 type predict (see Table, column 5) that for **5** the next two orbitals to be those nearly degenerate π-orbitals of the benzene ring which belong to the irreducible representations A_2 and B_1. This degeneracy should give rise to two very strongly overlapping bands. Accordingly we assign the second peak in the PE. spectrum of **5** to ionizations from these two orbitals (bands ② and ③). Our assignment of the a_2 orbital to a lower ionization potential than the b_1 orbital is based on simple arguments from perturbation theory as well as EHT-calculations (see Table). That bands ② and ③ are due to the ejection of an electron from a π-orbital is supported by the PE. spectrum of benzocyclobutenedione in which two bands are observed at 10.13 eV and 10.4 eV which are close in energy to bands ② and ③ of **5** and which are due to the ejection of an electron from the a_2 and b_1 orbitals [19].

Table. *Comparison between observed vertical ionization potentials of* **1** *to* **5** *with calculated orbital energies* (*EHT*). For **1** to **4** the calculated orbital energies are given only for the n-orbitals. The ionization potentials in brackets are estimated. All values are given in eV.

Compound	band	$I_{v,J}$	orbital	orbital energy	center of gravity
 **1** (C_{2v})	①	9.00	$b_2(n)$	–11.84	–13.29
	②	10.55	$a_1(n)$	–13.14	
	③	11.58	σ		
		(12.00)	$b_2(n)$	–14.90	
 **2** (C_2)	①	9.10	$b(n)$	–12.01	–13.18
	②	10.38	$a(n)$	–12.63	
	③	11.35	σ		
		(12.12)	$b(n)$	–14.90	
 **3** (C_s)	①	9.49	$a''(n)$	–12.18	–13.29
	②	10.60	$a'(n)$	–12.89	
	③	11.47	$a''(n)$	–14.79	
	④	12.10	σ		
 **4**	①	9.14	n	–12.09	–13.39
	②	10.60	n	–13.27	
	③	11.30	σ	–14.80	
	④	11.62			
		(11.85)	n		
 **5** C_{2v}	①	9.1	$b_2(n)$	–12.02	–13.23
	②	10.32	$a_2(\pi)$	–12.90	
	③	10.72	$b_1(\pi)$	–12.93	
	④	10.72	$a_1(n)$	–13.06	
	⑤	11.87	$b_2(n)$	–14.61	

Due to its steep ascent we assign band ④ of the PE. spectrum of **5** to the a_1 orbital; this is supported by its ionization potential (10.72 eV) which is slightly lower than the ionization potential of the corresponding band of **1**–**4**, as anticipated owing to the inductive effect of the benzene ring.

Band ⑤ of **5** we assign to the second b_2 combination of the $2p$-lone pairs on the oxygen atoms, based on semiempirical calculations and on the assumption that the MO's corresponding to the C–C and C–H bonds should be lower in energy in **5** than in the triketones **1**–**4** and also lower than the highest σ-MO in benzene (11.5 eV) [20].

Assuming that the center of gravity of the three lone pair combinations on the oxygen atoms in **1**–**5** stays approximately constant we obtain from **5** a value: $(9.10 + 10.72 + 11.87) : 3 = 10.56$ eV. This assumption is corroborated by the EHT-calculations, shown in the Table, column 6, which yield for the third n-orbital of **3** an ionization potential 11.6 eV, which is close to the value obtained for the third band (11.47 eV). For compound **1**, **2** and **4**, however, the band corresponding to the ionization from the third n-orbital is predicted by this assumption to be overlapped by σ-orbitals; the approximate position of the former is indicated by broken bars in Fig. 2.

We thank the *Fonds der Chemischen Industrie* and the *Otto Röhm Gedächtnisstiftung* for financial support.

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