The Vinylogous Tricarbonyl Chromophore. Violerythrine End Groups and Related Six-Membered Ring Compounds. Their Synthesis, Conformation, and Investigation by Photoelectron, UV, and NMR Spectroscopy and by Crystal Structure Analysis[1)]

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The synthesis of five- and six-membered rings **3a**, **4**, **5b**, **5c**, and **17a**, containing the structural moiety 3-pentene-1,2,5-trione, is described. The chromophoric properties of these vinylogous tricarbonyls together with related compounds are investigated. The conformation in solution, particularly the torsion angle ring/side-chain, can be derived from measurements of $^3J_{CH}$ coupling constants, NOE difference spectra, and force-field calculations. X-ray structure analyses of **11a**, **17a**, **18a**, and **35** afford geometries in the solid state. Ionization energies are determined by means of photoelectron spectroscopy. The theoretical calculations and interpretation of absorption spectra and colour are carried out using the models CNDO/S-CI and HAM/3.

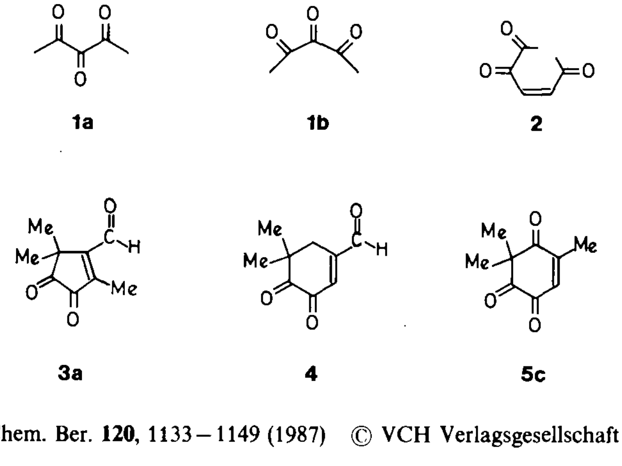
Der vinyloge Tricarbonyl-Chromophor. Violerythrin-Endgruppen und verwandte Sechsringverbindungen. Synthese, Konformation, Untersuchung mit Photoelektronen-, UV-, NMR-Spektroskopie und Röntgenstrukturanalyse[1)]

Die Synthese von ungesättigten Fünf- und Sechsringen, **3a**, **4**, **5b**, **5c** und **17a**, die das Strukturelement des 3-Penten-1,2,5-trions enthalten, wird beschrieben. Diese vinylogen Tricarbonyle werden zusammen mit verwandten Verbindungen auf ihre chromophoren Eigenschaften hin untersucht. Die Konformation in Lösung, insbesondere der Torsionswinkel Ring-Seitenkette, wird mit Hilfe von $^3J_{CH}$-Kopplungen, NOE-Differenzspektren und Kraftfeldrechnungen abgeleitet. Röntgenstrukturanalysen von **11a**, **17a**, **18a** und **35** liefern die Geometrie im festen Zustand. Die Ionisierungsenergien werden photoelektronenspektroskopisch bestimmt. Zur Berechnung und Interpretation der Absorptionsspektren und der Farbe werden die CNDO/S-CI- und die HAM/3-Methode verwendet.

As a result of both synthetic and spectroscopic studies the nature of vicinal triketones **1a** or **1b** has been determined[2)]. On the other hand, little information has been presented for vinylogous tricarbonyl compounds such as **2**, although the spectral properties of this chromophore are important in the interpretation of the colour of violerythrine[3a)], analogous norcarotinoid-diones[3b)], and of compounds containing the cyclohexenetrione chromogene. Recently an acoran antibiotic containing the chromophore **5c** was isolated from the fungus *Hemimycena cucullata*[3c)]. The tetraketo tautomer of astacene, which as of yet has not been investigated, may also be classified into this group[4)].

In this article we discuss the synthesis, conformation, light absorption, and spectroscopic characteristics of the polycarbonyl compounds **3**, **4**, and **5**, and of related compounds.

Scheme 1



Synthesis

Cyclopentenone **6** was employed as the starting material for the synthesis of carbonyl compounds with cyclopentene structure. Synthesis via **7**, **8**, and **9** was chosen after consideration of work by Kienzle and Minder[5)]. Oxidation of **9** with selenium dioxide gave deep red, ruby-like crystals of the aldehyde **3**. The cyclopentenone compounds **6** and **15** are also oxidised by SeO_2[6)]. **16**, however, can be directly produced from **3**. Phosphorane and phosphonate addition to **9** yields the ketone **10** and the ester **14**. Both **13** and **14** can be converted by SeO_2 into diketones.

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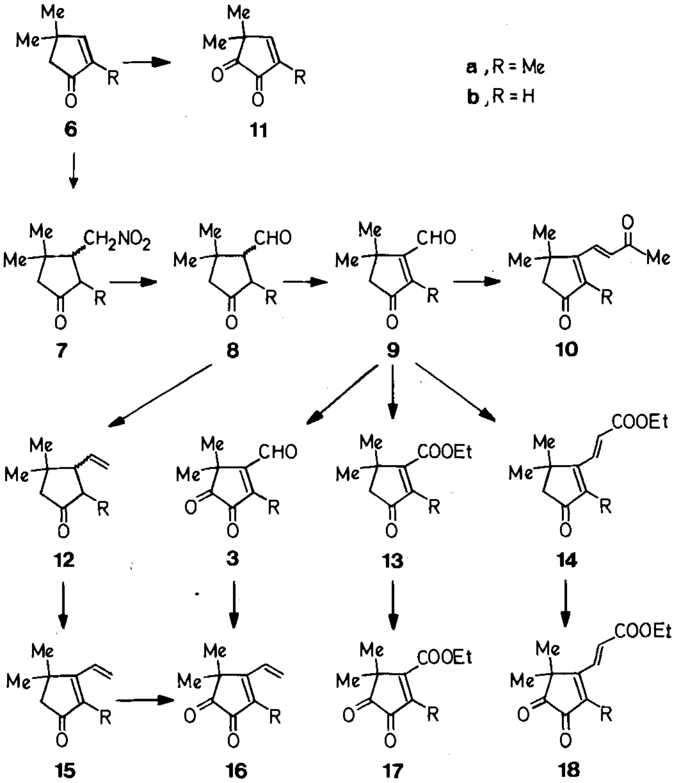
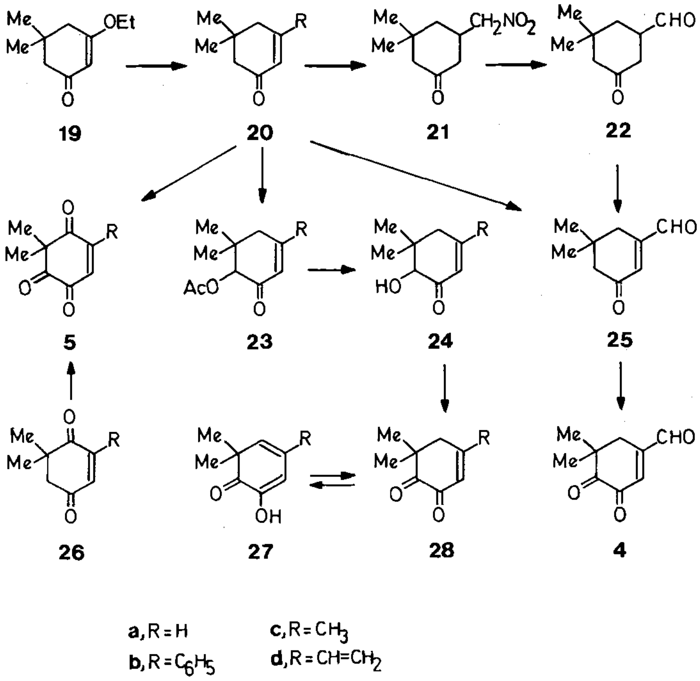
Scheme 2



Scheme 3



The synthesis of the cyclohexenedione **4** is in principle conceivable by a similar sequence of reactions and in practice it has been found that **4** can be produced from **19** via **22** and **25** with SeO_2. Although another method of preparation of **25** has been described[7], we found the ozonolysis of the vinyl compound **20d** to be the most suitable way to obtain **25**. α-Dione compounds **28** were expediently produced by the oxidation of **20** with lead tetraacetate, followed by hydrolysis and further oxidation with dimethyl sulfoxide/acetic anhydride. Whilst derivatives **b** and **c** may be obtained in the enol form **27** or in the keto form **28**, **28a** so far shows no tendency towards enol formation. The cyclohexenone compounds **20b** and **20c** are oxidised by SeO_2 directly to **5** and not to **28**, in the case of **20c**, however, the yield is only some 5%. The route via 1,4-dione **26c** was found to be more efficient[8].

The oxoionone compounds **31** and **32** were prepared via unsaturated aldehydes and subsequent Wittig reaction.

Conformational Studies

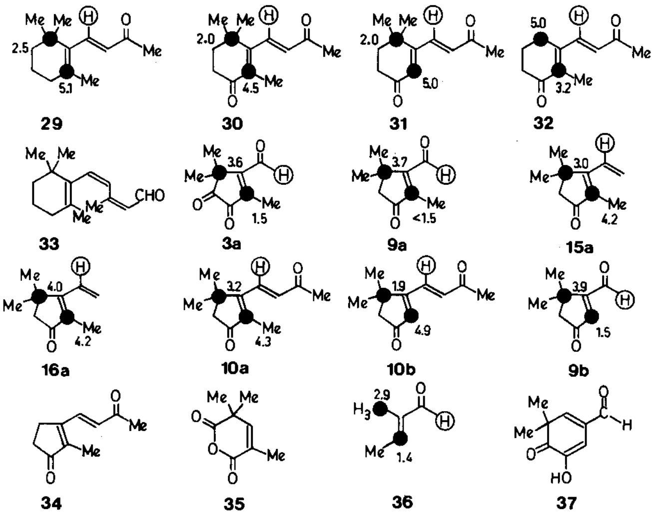
The conformation between the ring and the side chain is particularly important in the discussion of the chromophoric nature of carotinoids and of end groups with shortened side chains[9]. In general NMR[10], X-ray structural analysis[11], and theoretical models[12] are used to determine favoured conformations. Determination of the orientation of the side chain towards the ring is difficult because in solution a dynamic conformational equilibrium (*s-cis* vs. *s-trans*) and differing torsion angles (between 0° and 180°) may be present. It has been concluded from bathochromic shifts observed for five-membered carotinoids with respect to six-membered ring compounds that the five-membered ring is in a coplanar position vis à vis the side chain[3]. The X-ray structural analysis of 2-norvitamine A acid indicated a planar *s-trans* conformer[13]. By NOE difference technique it was shown that an equilibrium exists between *s-cis* and *s-trans* conformers in 2,2′-dinor-β,β-carotene-4,4′-dione[14]. Karplus et al. used both the NOE of methyl protons on the ring towards the olefinic protons 7-H and 8-H as well as the angular dependance of homoallyl coupling $^5J(\text{7-H/5-CH}_3)$ and $^5J(\text{7-H/4-H})$ in their conformational analyses[10,12].

As far as we are aware vicinal coupling $^3J(\text{7-H/C-1})$ or $^3J(\text{7-H/C-5})$ has not been used in conformational analysis. We established that it is possible to eliminate interfering coupling in compounds such as those discussed here by the use of double resonance and thus that reduced coupling constants ^3J_r can be obtained. In the case of a large decoupling power[15] these constants are proportional to the true constants $^3J_0$. The required coupling is thus obtained from the relationship $^3J_0 = {}^3J_r\,({}^1J_0/{}^1J_r)$. The experimental validity of this relationship can be verified against every molecule for which $^3J_0$ is known, either directly from the spectrum or from other measurements. For example: $^3J(\text{C-5/7-H}) = 5.0$ Hz in oxoionon **31** can be ascertained directly from the spectrum because $^3J(\text{C-5/3-H})$ is very small. It is assumed that similar relationships to those used for other ^3J couplings are valid for the dependancy on the angle of torsion of these ^3J couplings[16,17].

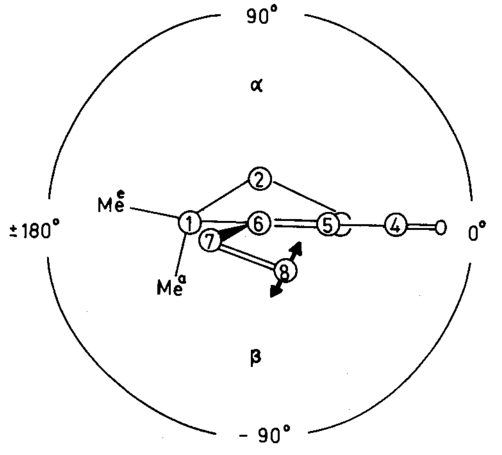
Cyclohexene and cyclopentene derivatives for which ^3J couplings have been determined are shown in Scheme 4. From these data it can be concluded that the *s-cis* conformation is preferred by **29**–**31** and **10b**. The *s-trans* conformation on the other hand will dominate in **32**, **3a**, **9a** and **9b**. **9b** may be compared with tiglinaldehyde (**36**). Force-field calculations for this compound predict an *s-trans* conformation (Tab. 1). The measured coupling constants (cf. **36**) agree well with the values for **9b**.

We interpret the results for **15a**, **16a** and **10a** as being due to the presence of a *s-cis,s-trans* conformer equilibrium.

Scheme 4



In order to further investigate the geometry of favoured conformations, the MMP1 programme from Allinger was used[18)]. Calculations were undertaken for the characteristic substituted compounds **30**–**32**, **10a**,**b** and **34**. Furthermore the conformations of β-ionone (**29**) and of the 7-*cis* derivative **33** were calculated. Both of these molecules habe been experimentally investigated by Honig et al. and Liu et al.[10)].



(1)

Koch (cited in ref.[11)]) and Gieren et al.[11)] established that two diastereomeric *s-cis* and two diastereomeric *s-trans* conformers have to be differentiated when considering the 6,7 rotation of a non-planar six-membered ring. These are *cis* α, *cis* β, *trans* α and *trans* β. This nomenclature is shown in (1). Only carbon atom C-2 diverges from the plane of the cyclohexenone ring (in this case above the plane).

The MMP1 results (relative energies in kcal/mol, torsion angle) for β-ionone (**29**) are: *cis* α 0.0, +50°; *cis* β 0.2, −50°; *trans* α 4.1, +175°; *trans* β 2.5, −140°. These are in excellent agreement with the measured ^3J coupling. For the 7-*cis* derivative **33** the following results were obtained: *cis* α 0.0, +50°; *cis* β 2.2, −40°; rotational barrier (*cis* α→ *cis* β) 10.0. This result also agrees very well with the barrier of $\Delta G^{\neq}$ = 11.4 kcal/mol reported by Liu et al.[10)].

Results for ten compounds are compiled in Table 1.

Table 1. MMP1 conformers of **9a**, **10a**, **b**, **13a**, **14a**, **30**–**32**, **34** and **36**. Φ (Degrees) is the angle of torsion about the single bond ring/side chain [see (1)]. The differentiation between α and β disappears in planar five-membered rings. E_{rel} in kcal/mol (kJ/mol)

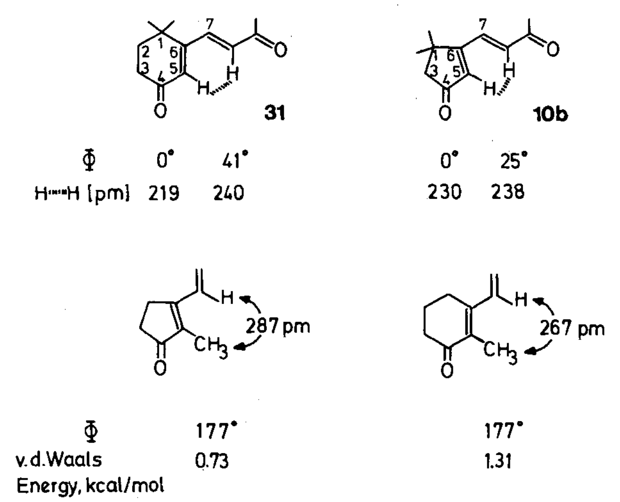
No.		Φ	E_{rel}	%
30	cis α	54	0.00 (0.00)	68.0
	cis β	−57	0.47 (1.96)	30.9
	trans α	163	4.95 (20.71)	0.1
	trans β	−136	2.47 (10.33)	1.0
31	cis α	41	0.00 (0.00)	79.8
	cis β	−44	0.90 (3.76)	17.6
	trans α	--	-- --	--
	trans β	−157	2.05 (8.57)	2.5
32	cis α	50	1.06 (4.43)	12.0
	cis β	−53	1.12 (4.69)	11.0
	trans α	--	-- --	--
	trans β	−164	0.00 (0.00)	77.0
9a	cis	0–25	2.97 (12.41)	0.6
	trans	180	0.00 (0.00)	99.4
10a	cis	46	0.36 (1.51)	35.0
	trans	168	0.00 (0.00)	65.0
10b	cis	25	0.00 (0.00)	61.0
	trans	175	0.26 (1.09)	39.0
13a	cis	19	1.81 (7.56)	5.1
	trans	180	0.00 (0.00)	94.9
14a	cis	51	0.36 (1.51)	35.0
	trans	169	0.00 (0.00)	65.0
34	cis	42	3.07 (12.84)	0.5
	trans	178	0.00 (0.00)	99.5
36	cis	0	3.22 (13.45)	0.4
	trans	180	0.00 (0.00)	99.6

These data significantly support the geometries derived from coupling constants. In addition these calculations show why the cyclopentene compounds are less distorted than the six-membered ring compounds. From Scheme 5 it can be seen that the non-bonding H···H repulsion at a dihedral angle of 0° in **31** is larger than that in **10b** and that the distortion must therefore be larger in **31** than in **10b**.

A similar situation exists for *s-trans* conformers (Scheme 5). At an angle Φ of 177° noticeably higher van der Waals energies result for the six-membered ring. Additionally, when a 1,1-dimethyl group is present this non-planar ring causes a steric repulsion with the pseudoequatorial 1-

methyl group, such that the side chain deviates towards the axial methyl group. Thus the *s-trans* minimum for **31** is on the *trans* β side. The same is true of 4-oxo-β-ionone (**30**). The interaction with the pseudoequatorial 1-methyl group also explains why the *cis* α form is favoured.

Scheme 5



^{1}H,^{1}H-NOE measurements are particularly informative for the determination of favoured conformations[10]. This method was used by Honig et al.[10] and Müllen et al.[10] to determine that the favoured conformation of β-ionone (**29**) has a distorted *s-cis* geometry. We have investigated the dione ester **18a** by the NOE difference technique to compare the conformation formed in solution with that found in the solid state (see next section).

The observed fractional Overhauser enhancements $f_{\text{irr}}^{\text{obs}}$ [where obs = observed proton α or β and irr = irradiated protons allylic methyl (all) or geminal methyl (gem)] for the resonance of the olefinic protons H_α and H_β (α and β with respect to the ester group) of **18a** are (at 400 MHz, $CDCl_3$, 25°C):

$$f_{\text{all}}^{\alpha} = 0.05 \qquad f_{\text{all}}^{\beta} = 0.16$$
$$f_{\text{gem}}^{\alpha} = 0.25 \qquad f_{\text{gem}}^{\beta} = 0.12$$

The interpretation was carried out according to the procedure of Schirmer, Noggle et al.[19] with the assumption that relaxation of the α and β protons was dominated by intramolecular dipole-dipole interactions, that all interactions had the same correlation time and finally, that the methyl groups could be treated as point dipoles. Under these conditions the relative Overhauser enhancements may be approximately written as (2).

$$\begin{aligned} f_i^{\alpha} &= \frac{1}{2}\,\frac{\langle r_{i\alpha}^{-6}\rangle}{R_\alpha} - \frac{1}{2}\,\frac{\langle r_{\alpha\beta}^{-6}\rangle}{R_\alpha}\,f_i^{\beta} \\ f_i^{\beta} &= \frac{1}{2}\,\frac{\langle r_{i\beta}^{-6}\rangle}{R_\beta} - \frac{1}{2}\,\frac{\langle r_{\alpha\beta}^{-6}\rangle}{R_\beta}\,f_i^{\alpha} \end{aligned} \qquad (2)$$

f_i^{α} is the fractional enhancement of H_α by irradiation of the i^{th} methyl group, $R_\alpha = \sum_k \langle r_{k\alpha}^{-6}\rangle$ (k = 3-CH_3, 5,5′-CH_3, H_β).

The results from (2) against the torsion angle between the ring and the side chain are shown in Fig. 1.

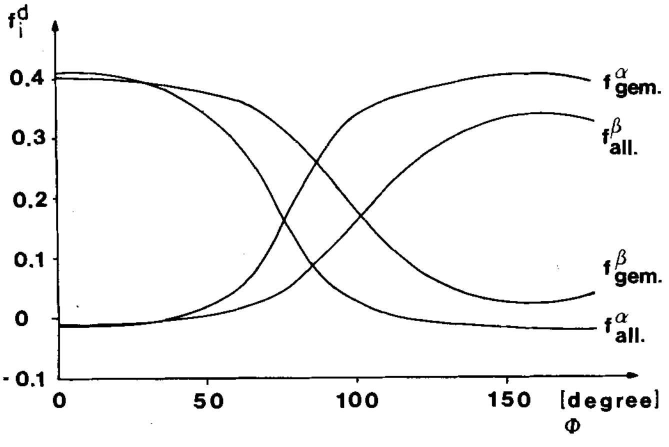


Figure 1. Calculated fractional Overhauser enhancements as a function of the torsion angle Φ (ring/side chain)

It is clear that a single conformation cannot account for the observed enhancements.

However if the 2:1 equilibrium found for **14a** in Table 1 is taken into consideration then the following values are obtained:

$$f_{\text{all}}^{\alpha} = 0.10 \qquad f_{\text{all}}^{\beta} = 0.22$$
$$f_{\text{gem}}^{\alpha} = 0.27 \qquad f_{\text{gem}}^{\beta} = 0.15$$

Although the absolute agreement is only moderate the trend is reproduced correctly. We assume that the deviations are due to the omission of further f_i^k terms in the approximate equation (2). It is, however, to be assumed that the relationships between two enhancements are better reproduced than absolute values. This is confirmed by the values in (3).

	$f_{\text{gem}}^{\alpha}/f_{\text{gem}}^{\beta}$	$f_{\text{all}}^{\alpha}/f_{\text{all}}^{\beta}$	$f_{\text{all}}^{\beta}/f_{\text{gem}}^{\beta}$	$f_{\text{all}}^{\alpha}/f_{\text{gem}}^{\alpha}$	
obs.	2.08	0.32	1.33	0.21	(3)
calcd.	1.80	0.45	1.47	0.37	

Crystal Structures of 11a, 17a, 18a, and 35[20]

Crystals of **11a** and **17a** were grown in thin-walled capillary tubes on a diffractometer (Syntex P 2_1 with modified[21] low-temperature attachment LT-1) from concentrated solutions in chloroform. The solutions were first quenched in a cold nitrogen stream and the polycrystalline materials obtained were then transformed into single crystals by miniature zone-melting[22] using a stream of warm gas (**11a**) or focused heat radiation (**17a**). A single crystal of **35** was obtained when focused heat radiation was applied to **11a**. Crystals of **18a** were grown from solution in diethyl ether. The crystallographic data and reflection intensities were measured with Mo-K_α radiation, graphite monochromator, and variable omega scan. Particulars of crystallography, diffractometry and refinement are given in Table 2.

Table 2. Crystallographic data and some numbers related to diffractometry and refinement

	11a	35	17a	18a
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
cell constants a/pm	647.5(4)	643.1(3)	835.5(4)	887.2(3)
b/pm	676.9(3)	664.9(3)	1939.2(6)	1212.7(4)
c/pm	902.1(5)	963.2(4)	687.0(1)	1167.5(3)
β/deg.	91.36(5)	90.74(3)	92.34(3)	96.50(2)
V/pm^3	$395.3 \cdot 10^6$	$411.8 \cdot 10^6$	$1112.2 \cdot 10^6$	$1248.1 \cdot 10^6$
space group; Z	$P2_1/m$; 2	$P2_1/m$; 2	$P2_1/c$; 4	$P2_1/n$; 4
calcd. density/$mg \cdot mm^{-3}$	1.430	1.243	1.255	1.257
measuring temp./°C	-7	-85	-40	-103
$2\theta_{max}$ (MoKα)/deg.	60	60	50	80
indep. reflns: obsd. $(\lvert F_o \rvert \geq 3.92\sigma_F)$; total	829; 1239	805; 1288	1245; 1954	2355; 3816
varied parameters	80	86	192	239
R: obsd.; total	0.058; 0.082	0.053; 0.085	0.071; 0.106	0.058; 0.091
R_w: obsd.; total	0.068; 0.071	0.061; 0.065	0.077; 0.082	0.087; 0.072
residual el. density min...max/$10^{-6} e \cdot pm^{-3}$	-0.16...0.26	-0.21...0.27	-0.29...0.32	-0.22...0.25

Table 3. Atomic parameters of **11a** with standard deviations in parentheses. The equivalent isotropic thermal parameters (in $10^2 pm^2$) of the C and O atoms were calculated from the anisotropic U_{ij} by: $U_{eq} = (1/3)(U_{11}a^{*2}a^2 + \cdots + U_{23}b^*c^*bc \cdot \cos\alpha)$

Atom	x	y	z	U_{eq}
C(1)	0.4879(3)	0.2500	0.2225(3)	5.08(7)
C(2)	0.4752(3)	0.2500	0.0535(3)	4.83(7)
C(3)	0.2554(3)	0.2500	0.0119(3)	4.88(7)
C(4)	0.1471(3)	0.2500	0.1348(3)	5.40(8)
C(5)	0.2696(3)	0.2500	0.2783(3)	5.88(8)
C(6)	0.1787(6)	0.2500	-0.1441(4)	7.52(12)
C(7)	0.2320(4)	0.0587(6)	0.3658(3)	10.66(12)
O(1)	0.8485(3)	0.2500	0.2954(2)	7.88(8)
O(2)	0.6236(2)	0.2500	-0.0261(2)	7.57(7)

Table 4.
Atomic parameters of **35** (for details see legend of Table 3)

Atom	x	y	z	U_{eq}
C(1)	0.4821(4)	0.2500	0.2557(3)	4.62(9)
C(2)	0.5328(3)	0.2500	0.0051(3)	4.23(6)
C(3)	0.7591(3)	0.2500	0.0246(2)	3.67(7)
C(4)	0.8372(3)	0.2500	0.1523(3)	3.96(8)
C(5)	0.7142(3)	0.2500	0.2828(2)	4.19(8)
C(6)	0.8831(4)	0.2500	-0.1062(3)	5.07(10)
C(7)	0.7681(4)	0.4404(5)	0.3672(3)	6.71(9)
O	0.4079(2)	0.2500	0.1210(2)	4.74(6)
O(1)	0.3534(3)	0.2500	0.3425(2)	8.14(10)
O(2)	0.4447(3)	0.2500	-0.1045(2)	7.44(9)

Table 5.
Atomic parameters of **17a** (for details see legend of Table 3)

Atom	x	y	z	U_{eq}
C(1)	1.2395(5)	0.4676(2)	0.2505(8)	5.2(2)
C(2)	1.0604(5)	0.4816(2)	0.2548(8)	4.6(1)
C(3)	0.9789(4)	0.4147(2)	0.2464(5)	3.5(1)
C(4)	1.0908(4)	0.3647(2)	0.2357(5)	3.4(1)
C(5)	1.2643(4)	0.3905(2)	0.2317(5)	4.0(1)
C(6)	0.8014(5)	0.4128(2)	0.2506(7)	5.3(2)
C(7)	1.3409(7)	0.3764(3)	0.0370(9)	6.7(2)
C(8)	1.3658(6)	0.3645(2)	0.4082(7)	8.8(2)
C(9)	1.0629(5)	0.2884(2)	0.2223(5)	3.8(1)
C(10)	0.8727(5)	0.1979(2)	0.2386(8)	4.5(1)
C(11)	0.6968(5)	0.1908(2)	0.2668(6)	6.4(2)
O(1)	1.3430(4)	0.5109(2)	0.2583(5)	8.7(2)
O(2)	1.0003(4)	0.5384(1)	0.2637(5)	7.3(1)
O(3)	1.1644(3)	0.2482(1)	0.1868(5)	6.9(1)
O(4)	0.9102(3)	0.2713(1)	0.2513(4)	4.2(1)

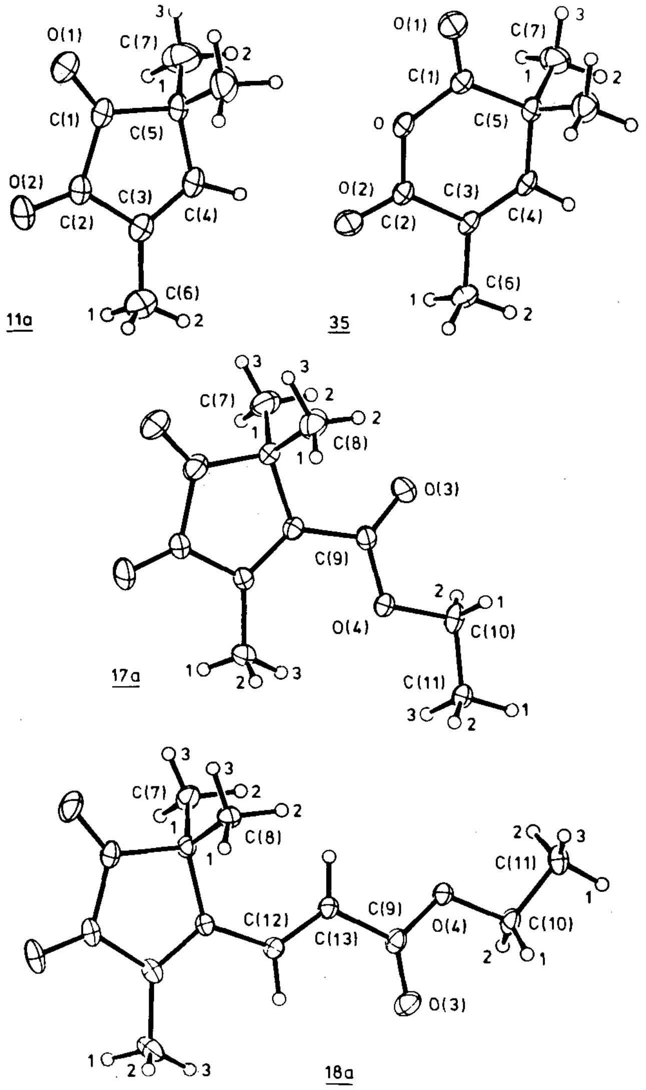


Figure 2. Molecules with atomic thermal vibration ellipsoids (25% probability). The ethoxy group in **18a** is shown with its 80% orientation only

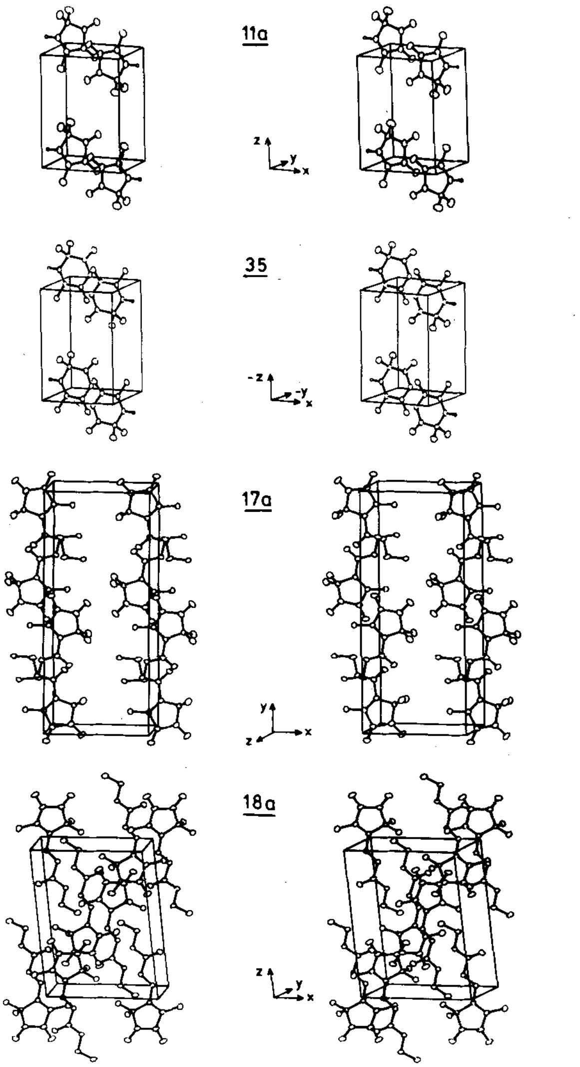


Figure 3. Packing of the molecules in their unit cells. Of the H atoms, only 4-H of **11a** and **35** is shown

Table 6. Atomic parameters of **18a**. The atoms C(10 s), C(11 s), and O(4 s) are the split atoms with 20% occupancy. (For further details see legend of Table 3)

Atom	x	y	z	U_{eq}
C(1)	0.7115(2)	0.6644(2)	-0.2668(2)	4.01(6)
C(2)	0.8749(3)	0.7029(2)	-0.2687(2)	3.93(6)
C(3)	0.9498(2)	0.6901(2)	-0.1512(2)	3.46(6)
C(4)	0.8506(2)	0.6449(1)	-0.0830(1)	2.83(5)
C(5)	0.6929(2)	0.6210(2)	-0.1465(1)	3.12(5)
C(6)	1.1116(3)	0.7228(2)	-0.1212(2)	5.21(8)
C(7)	0.5637(2)	0.6850(2)	-0.0998(2)	4.48(7)
C(8)	0.6574(2)	0.4976(2)	-0.1564(2)	4.08(6)
C(9)	0.8750(2)	0.5518(2)	0.2323(2)	3.72(6)
C(10)	0.8259(3)	0.4946(3)	0.4168(2)	4.03(8)
C(11)	0.6957(4)	0.4471(3)	0.4712(2)	5.77(11)
C(12)	0.8955(2)	0.6191(2)	0.0377(1)	3.08(5)
C(13)	0.8093(2)	0.5768(2)	0.1124(1)	3.46(6)
O(1)	0.6144(2)	0.6693(2)	-0.3476(1)	6.71(7)
O(2)	0.9284(2)	0.7365(1)	-0.3535(1)	5.73(6)
O(3)	1.0058(2)	0.5630(1)	0.2699(1)	5.03(5)
O(4)	0.7728(2)	0.5189(2)	0.2966(1)	3.69(5)
C(10s)	0.788(2)	0.425(1)	0.392(1)	5.3(4)
C(11s)	0.748(1)	0.504(1)	0.4772(8)	6.2(4)
O(4s)	0.7468(7)	0.4813(6)	0.2757(5)	4.1(2)

Table 7. Bond lengths between non-H atoms (pm)

Bond	11a	35	17a	18a
C(1)-C(2)	152.5(3)		152.3(6)	152.5(3)
C(2)-C(3)	146.3(3)	146.6(3)	146.5(5)	146.3(3)
C(3)-C(4)	132.6(3)	132.2(3)	135.0(5)	136.6(3)
C(4)-C(5)	150.2(3)	149.5(3)	153.6(5)	153.5(2)
C(5)-C(1)	151.2(3)	151.2(3)	151.5(5)	152.6(3)
C(1)-O		137.6(3)		
C(2)-O		138.3(3)		
C(1)-O(1)	120.6(3)	118.5(3)	120.5(5)	120.5(2)
C(2)-O(2)	121.3(3)	119.1(3)	121.4(4)	121.6(3)
C(3)-C(6)	148.1(4)	149.9(4)	148.5(5)	149.2(3)
C(5)-C(7)	153.9(4)	154.2(3)	153.2(7)	153.4(3)
C(5)-C(8)			152.6(6)	153.1(3)
C(4)-C(9)			149.9(5)	
C(9)-O(3)			118.6(5)	120.0(2)
C(9)-O(4)			134.1(5)	130.4(3)
O(4)-C(10)			146.1(4)	145.9(3)
C(10)-C(11)			149.7(6)	149.5(4)
C(4)-C(12)				145.5(2)
C(12)-C(13)				132.7(3)
C(13)-C(9)				148.6(2)

Table 8. Bond angles between non-H atoms (deg.)

Bond angle	11a	35	17a	18a
C(1)-C(2)-C(3)	106.6(2)		107.2(3)	106.6(2)
C(2)-C(3)-C(4)	108.4(2)	118.9(2)	108.5(3)	109.5(2)
C(3)-C(4)-C(5)	116.2(2)	125.7(2)	115.0(3)	114.0(1)
C(4)-C(5)-C(1)	101.1(2)	112.7(2)	100.8(3)	101.0(1)
C(5)-C(1)-C(2)	107.7(2)		108.4(3)	108.7(1)
C(5)-C(1)-O		119.5(2)		
C(1)-O-C(2)		124.3(2)		
O-C(2)-C(3)		118.6(2)		
O(1)-C(1)-C(5)	127.6(2)	125.1(2)	126.2(4)	126.5(2)
O(1)-C(1)-C(2)	124.7(2)		125.3(4)	124.8(2)
O(1)-C(1)-O		115.4(2)		
O(2)-C(2)-C(1)	124.5(2)		124.9(3)	125.0(2)
O(2)-C(2)-O		116.2(2)		
O(2)-C(2)-C(3)	128.9(2)	125.0(2)	127.8(4)	128.4(2)
C(6)-C(3)-C(2)	123.1(2)	115.5(2)	119.0(3)	121.0(2)
C(6)-C(3)-C(4)	128.5(2)	125.5(2)	132.6(3)	129.5(2)
C(7)-C(5)-C(4)	110.8(1)	109.0(1)	112.7(3)	114.2(1)
C(7)-C(5)-C(1)	109.3(1)	107.8(1)	108.3(3)	108.4(2)
C(8)-C(5)-C(4)			111.9(3)	112.9(1)
C(8)-C(5)-C(1)			109.4(3)	108.0(1)
C(7)-C(5)-C(7')	114.6(3)	110.4(2)		
C(7)-C(5)-C(8)			112.9(3)	111.4(2)
C(9)-C(4)-C(3)			127.3(3)	
C(9)-C(4)-C(5)			117.7(3)	
O(3)-C(9)-C(4)			123.5(3)	
O(4)-C(9)-C(4)			112.4(3)	
O(3)-C(9)-O(4)			124.1(3)	122.0(2)
C(10)-O(4)-C(9)			115.8(3)	116.4(2)
C(11)-C(10)-O(4)			106.9(3)	107.8(2)
C(12)-C(4)-C(3)				121.8(2)
C(12)-C(4)-C(5)				124.2(2)
C(13)-C(12)-C(4)				127.3(2)
C(9)-C(13)-C(12)				120.3(2)
O(3)-C(9)-C(13)				125.5(2)
O(4)-C(9)-C(13)				112.4(2)

Two modifications of **17a** were observed. X-ray powder exposures using the Guinier-Simon technique[23)] showed a transformation temperature of 0°C. Crystals of the monoclinic low-temperature form, the structure of which is described in this paper, tend to be twinned across the (100) plane. The high-temperature form is orthorhombic with space group *Pbcm*.

Calculation of the structures was performed using the programme system SHELXTL[24)] on a Data General Eclipse S/200 minicomputer. The phase problems were solved by direct methods. The H atoms were located in electron density difference maps and refined with the other atoms. Only the H atoms at C-6 of **18a** were generated by structural modelling and refined as a rigid group. The ethoxy group of **18a** came out with an 80:20 twofold disorder. The molecules of the four crystal structures and their atomic thermal vibration ellipsoids[25] are shown in Figure 2. Stereoscopic packing diagrams with unit cells are shown in Figure 3. The atomic parameters are listed in Tables 3 to 6, the bond lengths and bond angles of the C and O atoms in Tables 7 and 8[26].

The molecules of **11a** and **35** lie on mirror planes of the space groups, those of **17a** and **18a** are in general positions. The structure determination of **35** is the first one of a glutaconic anhydride, which, in contrast to other derivatives of known crystal structures[27-29], has no substituents capable of conjugation.

Comparison between the Structures in Solution and in the Crystalline State

The maximum distances of the atoms of the five-membered rings of **11a**, **17a**, and **18a** from their best planes are 0.0, 1.5(4) for atom C-5, and 2.2(3) pm for C-1. The torsional angles between the vicinal keto groups are 0.0, 1.2(7), and 4.8(4)°, respectively. In all these molecules the single-bond distances C(1)−C(2) and C(2)−C(3), resp., are evidence *against* an appreciable conjugation between the vicinal keto groups and *for* an interaction of this kind between the keto group C(2)−O(2) and the double bond C(3)−C(4). The latter point is also true for **35**. For **17a** and **18a** the conjugation can be traced to the carbonyl function in the side chain; the longer the conjugative system, the shorter is the single bond between the ring and the side chain. The conformation of this bond is in both molecules *s-trans* with respect to the adjacent double bonds, the torsion angles are 169.3(4) and 179.0(2)°, respectively. There are no unusually short intermolecular distances.

In contrast to that, the chloroform solution of **18a** displays a dynamic equilibrium between an *s-trans* and an *s-cis* conformer. This equilibrium is supported by the magnitude of ^3J(C,H) coupling constants, force-field calculations as well as by NOE difference measurements. Why in the solid state only the *s-trans* conformer prevails, can presumably be traced back to the smaller deviation from planarity of this conformer (cf. the torsion angles of **14a** and the related five-membered ring system **10a** according to MMP1, Tab. 1).

Photoelectron Spectra

He(Iα) photoelectron spectra of several compounds are shown in Figure 4. Ionization energies, I_j^m, and the assignments according to HAM/3[30] and MINDO/3[31] are given in Table 9.

Unsaturated five- and six-membered ketones **11a**, **16a**, **26**, **27b**, and **28a, b, c** shall now be considered. The first two PE bands of isophorone (**20c**) arising from n_O^{-1} and π^{-1} processes can be used as a starting point[33-36]. The inclusion of a second carbonyl group results in either 1,2-dione **28c** or 1,4-dione **26c**. The reason why the two spectra are different is obvious. In 1,2-dione **28c** the large Δn split of 1.62 eV results in a large separation of the n-bands whereas in 1,4-dione **26c** the split of 0.32 eV is relatively small[37,38].

Comparison with *p*-benzoquinone is particularly interesting as differing orbital sequences for the n and π levels have been suggested[39-44]. The π ionization energy was both expected and found to be similar for compounds **26c** and **28c** (10.14 and 9.98 eV) and hence the sequence of the n levels could be established.

The splitting of **26c** (Δn = 0.32 eV) is in accord with the sequence $n_- > n_+ > \pi > \pi$ for *p*-benzoquinone.

The extension of the conjugation via a vinyl or phenyl side chain (as in **16a** and **28b**) results in the expected additional π bands in the lower energy region of the spectrum. Comparison between the two tautomers **27b** and **28b** should also be given careful consideration. It is scarcely surprising that keto-enol tautomerism is seen in the PE spectrometer (at temperatures ca. 150°C) since it is evident that such temperatures (Kugelrohr distillation at 150°C) accelerate the conversion of the keto into the enol form. At first, when investigating **28b**, the spectrum of the diketo form may be recorded but after a short while only the spectrum of the enol form **27b** can be obtained. The latter exhibits the characteristic destabilized π MO at 8.0 eV. This energy is reproduced excellently by both HAM/3 and MINDO/3.

The introduction of yet another carbonyl group gives rise to vinylogous tricarbonyls. The structure of such compounds is illustrated well by examples **3a** and **5c**. Comparison of the spectra of these two compounds with **11a** and **28c** allows the differences to be summarized in the following way:

a) In the region between 10 and 11 eV a new band is present which can be assigned to the n_O^{-1} process.

b) The ionization energies arising from n_+^{-1}, π^{-1}, and n_-^{-1} processes are increased inductively by the additional carbonyl group. The stabilization of **5c**, however, is larger than for **3a** because in the latter compound the increase in new σ orbitals is larger than that for the former.

c) The Δn split for the α-dicarbonyl chromophore [$I(n_-) - I(n_+)$] remains practically unchanged by increased carbonyl conjugation. It is noticeably larger for the five-membered ring **3a** than for the six-membered ring system **5c** (1.96 vs. 1.66 eV).

Compared with the aldehyde **3a** the ethoxycarbonyl group in **17a** causes no inductive stabilization.

The extent of the π conjugation in **18a** is best demonstrated by considering the distance between n_+ and the first π band. In **11a** this distance Δn_+-π was found to be 1.09 eV whilst for **18a** it is only 0.6 eV.

The aldehyde **4** causes a particular problem, in that its PE spectrum shows not only the characteristic bands associated with the tricarbonyl chromophore at 9.25, 10.35, 10.65, and 10.95 eV but also two smaller peaks at 8.75 and 9.85 eV. These peaks are not due to contaminants. It is thus assumed that they are caused by a tautomeric dienol compound **37** formed during recording the spectrum. A good part of this hypothesis is provided by the PE spectrum, calculated for this dienol compound **37** with MNDO-optimized geometry [4-formyl-2-hydroxy-6,6-dimethyl-2,4-cyclo-

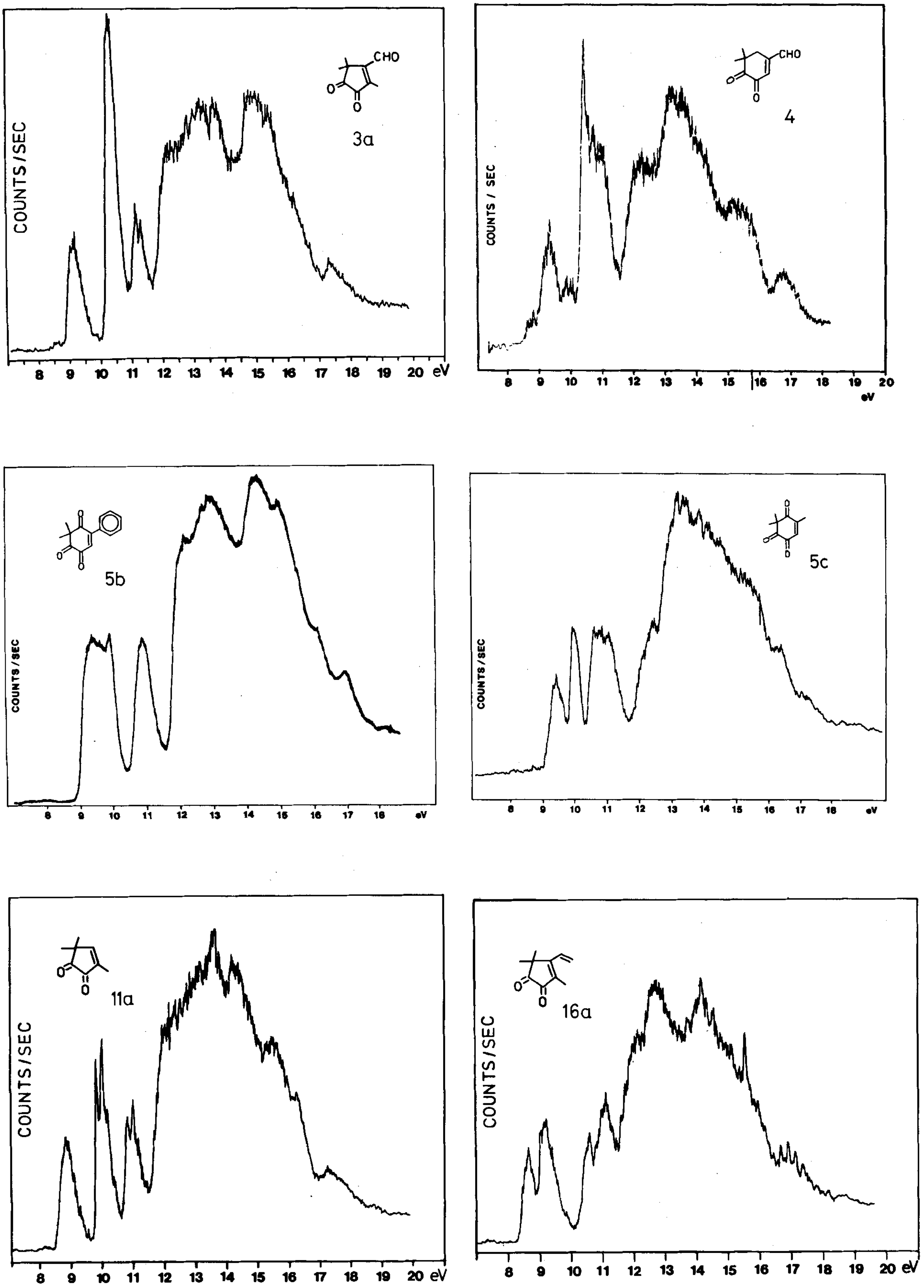


Figure 4. He(Iα) Photoelectron spectra

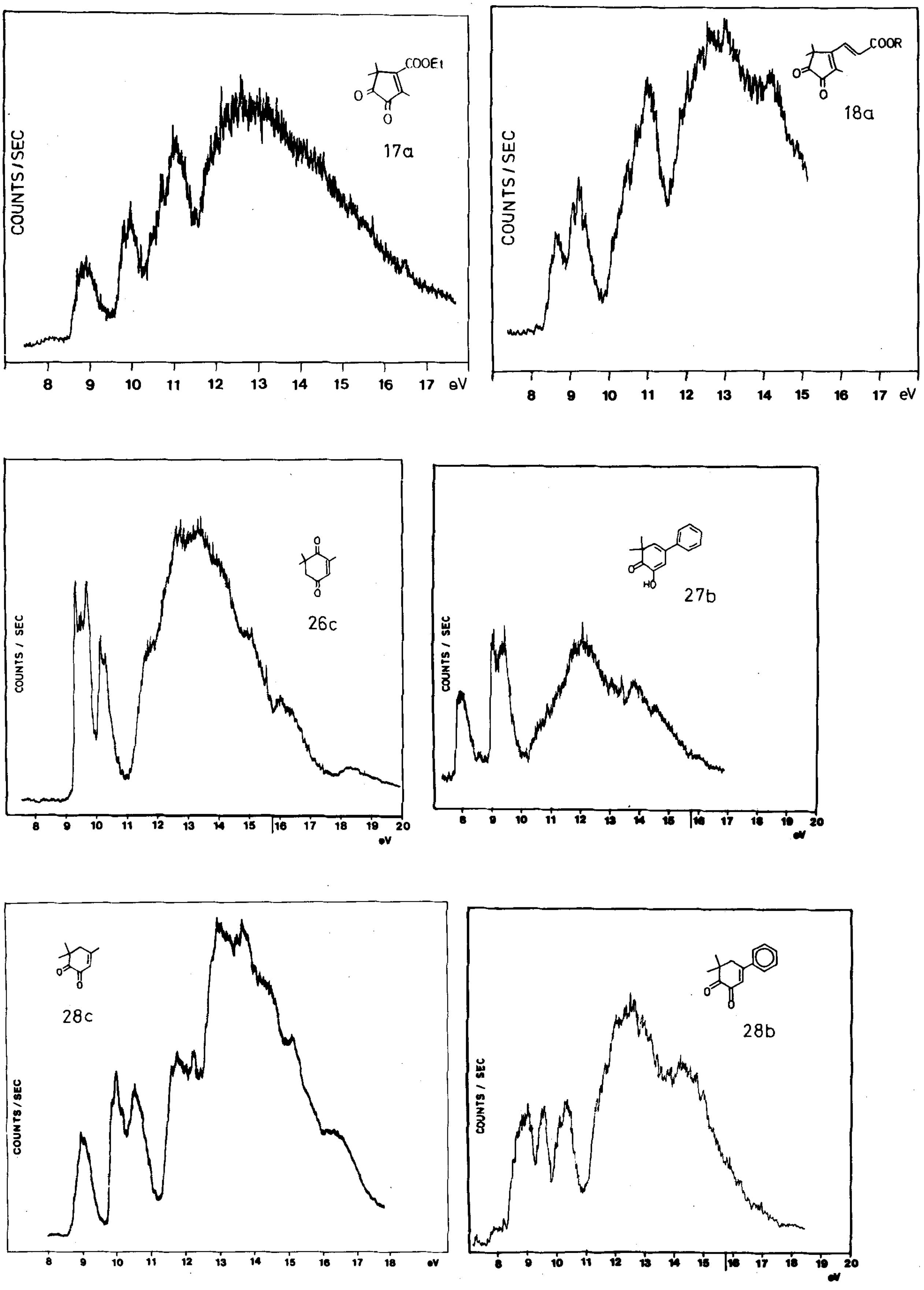


Figure 4 (*continued*)

Table 9. Ionization energies (maxima) I_j^m in eV. Error: ±0.03, ±0.05, or ±0.1, resp., if two decimals are given, if the second decimal place is given as a subscript, or if only one decimal place is given. Assignment ($\varepsilon_i = -I_j^m$): HAM/3[30] and MINDO/3[31]. Calculations are based on MNDO[32] optimized structures

No.	I_i^m	Assignments		
		Character	HAM/3	MINDO/3
3a	9.30	n_+	9.08	9.07
	10.45	n_O	9.66	10.58
		$\tilde{\pi}$	10.37	10.30
	11.26	n_-	11.04	11.14
4	9.25	n_+	9.07	9.29
	10.35	n_O	9.57	10.33
	10.65	$\tilde{\pi}$	10.52	10.78
	10.95	n_-	10.78	11.37
5b	9.4	n_+	9.00	9.05
	~9.8	$\tilde{\pi}$	9.17	9.16
		$\tilde{\pi}_{ar}$	9.21	9.44
	9.90	n_O	10.10	9.38
	10.90	n_-	10.60	10.52
		$\tilde{\pi}$	10.80	11.16
5c	9.44	n_+	9.29	9.35
	10.02	n_O	10.09	9.91
	10.8	$\tilde{\pi}$	10.45	10.70
	11.1	n_-	10.89	11.05
11a	9.05	n_+	8.69	8.93
	10.14	$\tilde{\pi}$	9.99	10.05
	11.10	n_-	10.62	10.92
16a	8.76	n_+	8.75	8.83
	9.24	$\tilde{\pi}$	9.09	9.29
	10.68	n_-	10.53	10.70 10.83 σ
	11.18	$\tilde{\pi}$	10.89	11.35
17a	8.94	n_+	8.89	9.04
	10.04	$\tilde{\pi}$	10.02	10.31
	10.5	n_O	10.17	10.49
	~11.2	$\tilde{\pi}_O$	10.72	11.12
		n_-	10.76	10.95
18a	8.73	n_+	8.61	9.03
	9.33	$\tilde{\pi}$	9.22	9.64
	10.6	n_O	9.74	10.34 10.97 σ
	10.8	n_-	10.43	11.02
	11.0	$\tilde{\pi}_O$	10.24	11.05
26c	9.34	n_-	9.44	9.39
	9.66	n_+	9.81	9.97
	10.14	$\tilde{\pi}$	10.33	10.42
27b	8.0	$\tilde{\pi}$	7.84	8.24
	9.00	$\tilde{\pi}_{ar}$	8.92	9.17
	9.5	n_O	9.02	9.21
		$\tilde{\pi}_{ar}$	9.05	9.38
28a	9.00	n_+	8.88	9.04
	10.3	$\tilde{\pi}$	10.00	10.44
	10.5	n_-	10.53	10.64
28b	9.0	n_+	8.48	8.88
		$\tilde{\pi}$	8.94	9.10
	9.60	π	9.36	9.59
	10.6	n_-	10.03	10.12
		$\tilde{\pi}$	10.21	10.59
28c	8.90	n_+	8.70	8.98
	9.98	$\tilde{\pi}$	9.77	10.18
	10.52	n_-	10.35	10.48

hexadien-1-one, MINDO/3: I_1 = 8.86 eV (π), I_2 = 9.60 eV (n_O ketone) and I_3 = 9.96 eV (n_O aldehyde)].

UV-VIS Spectra

UV-VIS spectral data for the dione compounds **28c**, **11a** and for the tricarbonyl compounds **3a**, **4**, **5c**, **17a**, and **18a** are given in Table 10.

CNDO/S-CI calculations were carried out for all seven molecules[45]. The geometry was optimized using MNDO[32]. In the case of five-membered rings planar conformations are obtained but varying local minima occurred for the six-membered ring dione compounds according to the starting point of the calculation. For example, the resulting geometry of **28c** is largely planar, when starting with a planar conformation (the calculated torsion angle $\Theta_{CO/CO}$ between the carbonyl groups is ca. 1°). If however the optimization is carried out on a distorted arrangement the optimized form is also distorted and $\Theta_{CO/CO} \approx 35°$. The distorted conformation of **28c** is, according to the MNDO model, 3.4 kcal mol^{-1} (14.2 kJ mol^{-1}) more stable than the planar conformer. The results of CNDO/S-CI calculations for such cases are shown in Table 10.

Cyclopentendione **11a** exhibits two n-π* transitions at 20576 and 31446 cm^{-1} (486 and 318 nm). These excited states should be described as B_2 and A_2 in the C_{2v} symmetry of the synperiplanar $(CO)_2$ chromophore. The experimental energy difference between these two singlet states is 1.34 eV and the value calculated by CNDO/S-CI is 1.24 eV. These results are in good agreement with the values calculated for synperiplanar glyoxal by Hug et al.[46] and Arnett et al.[47] using CNDO-CI.

On comparison with the six-membered dione **28c** five-membered **11a** shows a bathochromic shift of the long wavelength absorption band and an excellent agreement to the calculated results (for the distorted geometry of **28c**) is achieved. This comparison shows why six-membered dione compounds exhibit a hypsochromic shift compared to five-membered diones. Whilst the latter compounds are planar,

Table 10. UV-VIS spectral data for dicarbonyl and tricarbonyl compounds. Solvent: CH_3CN, in the case of **4** and **5c** $CHCl_3$. CNDO/S-CI calculations with 40 singly excited configurations. a) distorted geometry, b) distorted six-membered ring with planar $(CO)_2$ chromophore (see text), c) MNDO optimized with crystal geometry as starting point: $\Theta(CO/CO) = 0.3°$, $\Theta((CO)_2/C=C) = 13.5°$, $\Theta(C=C/CO) = 27.5°$, d) crystal geometry[51]

No.	λ_m (nm)	log ε	CNDO/S–CI (λ, f, % config.)
3a	550	1.27	491, 0.00003, 57% $n_+-\pi_1^*$, 24% $n_+-\pi_2^*$
	380	1.30	365, 0.00057, 40% $n_0-\pi_1^*$, 21% $n_0-\pi_3^*$
	289	3.83	327, 0.00020, 22% $n_+-\pi_4^*$, 14% $n_+-\pi_3^*$
	277	3.74	243, 0.60000, 88% $\pi-\pi_1^*$,
	258	3.47	
4	474	1.27	a) 440, 0.00043, 44% $n_+-\pi_1^*$, 24% $n_+-\pi_2^*$
	324	2.23	364, 0.00015, 42% $n_0-\pi_1^*$, 20% $n_0-\pi_3^*$
	258	4.13	322, 0.00064, 17% $n_+-\pi_2^*$, 17% $n_+-\pi_4^*$
			226, 0.34000, 44% $n_+-\pi_1^*$, 23% $\pi-\pi_1^*$
			b) 464, 0.00005, 55% $n_+-\pi_1^*$
			367, 0.00029, 38% $n_0-\pi_1^*$
			335, 0.00001, 21% $n_+-\pi_2^*$
			219, 0.86000, 94% $\pi-\pi_1^*$
5c	446	1.40	c) 447, 0.00022, 51% $n_+-\pi_1^*$
	338	1.71	346, 0.00026, 42% $n_0-\pi_1^*$
	251	4.03	327, 0.00011, 20% $n_--\pi_1^*$
			222, 0.37000, 39% $n_+-\pi_1^*$, 32% $\pi-\pi_1^*$
			d) 410, 0.00051, 36% $n_+-\pi_1^*$
			387, 0.00290, 39% $n_0-\pi_1^*$
			308, 0.03300, 37% $\pi-\pi_1^*$
11a	486	1.39	481, 0.00004, 75% $n_+-\pi_1^*$
	318	1.44	324, 0.00011, 31% $n_+-\pi_3^*$, 20% $n_+-\pi_2^*$
	273	3.72	232, 0.29000, 92% $\pi-\pi_1^*$
17a	510	1.36	494, 0.00003, 64% $n_+-\pi_1^*$, 24% $n_+-\pi_2^*$
	372	1.64	321, 0.00050, 21% $n_+-\pi_2^*$, 24% $n_+-\pi_4^*$
	334	1.75	287, 0.00080, 33% $n_0-\pi_1^*$, 19% $n_0-\pi_4^*$
	284	3.81	243, 0.49000, 95% $\pi-\pi_1^*$
18a	513	1.62	461, 0.00003, 51% $n_+-\pi_1^*$, 40% $n_+-\pi_2^*$
	326	4.29	300, 0.00100, 20% $n_+-\pi_3^*$, 22% $n_+-\pi_5^*$
			278, 1.00000, 97% $\pi-\pi_1^*$
28c	425	1.38	a) 426, 0.00038, 30% $n_+-\pi_1^*$, 32% $\pi-\pi_1^*$
	332	1.38	328, 0.00010, 14% $n_--\pi_1^*$
	261	4.12	218, 0.47000, 60% $n_+-\pi_1^*$, 25% $\pi-\pi_1^*$
			b) 455, 0.00006, 70% $n_+-\pi_1^*$
			336, 0.00002, 19% $n_+-\pi_2^*$
			220, 0.55000, 94% $\pi-\pi_1^*$

even in respect of their conjugated side chains (see structural data of **11a**, **17a**, and **18a**), six-membered cyclic diones have a distorted geometry. This distortion has practically no effect on the n_+ ionization energy (Table 9) although it must greatly influence the π_+^* orbital energies. This relationship between CO–CO dihedral angle and transition energy is well documented for saturated dione compounds[48,49].

The consequence of introducing a double bond into a saturated five-membered cyclic dione is different to that observed for the analogous six-membered ring compound.

For five-membered compounds such as 3,3,5,5-tetramethyl-1,2-cyclopentadione (TMCP)[48,49], which is already planar, an additional double bond has no further bathochromic effect. The corresponding six-membered compound 3,3,6,6-tetramethyl-1,2-cyclohexadione (TMCH)[49] has two CO groups which are distorted by 42° to one another, such that a conjugated double bond can cause the molecule to become more planar. This bathochromic effect due to a double bond in a six-membered ring dione is made particularly obvious by the comparison of TMCP with **11a** and of TMCH with **28c**.

$$\begin{array}{ccc} \text{TMCP}^{49)} & \textbf{11a} & \\ \lambda_m = 493\ \text{nm} & \lambda_m = 486\ \text{nm} & \Delta\lambda = -7\ \text{nm} \\ \text{TMCH}^{49)} & \textbf{28c} & \\ \lambda_m = 372\ \text{nm} & \lambda_m = 425\ \text{nm} & \Delta\lambda = 53\ \text{nm} \end{array} \qquad (4)$$

The spectral properties of the vinylogous tricarbonyl chromophore are determined by the n_+-π^* transition. The importance of geometry is discussed below for **3a**, **4**, and **5c**. Trione **3a** exists as the planar *s-trans* conformer (cf. **9a** in Table 1 and the X-ray analysis of **17a**). Compound **4** is optimized in the MNDO model with a distorted $(CO)_2$ chromophore (torsion angle 39°). The aldehyde group can exist in either the *s-trans* or the *s-cis* conformation and the heat of formation, calculated by MNDO, for either conformer is practically the same. MMP1 calculations for **4** yield a torsion angle for $(CO)_2$ of 46°[50]. According to X-ray structural analysis the triketo compound **5c**[51] exists as a distorted six-membered ring with an almost planar $(CO)_2$ chromophore (torsion angle 6.3°). The third CO group, however, is not planar with respect to the conjugated double bond (i.e. 180°) but rather has a torsion angle equal to 158.7°. The calculated conformation in solution, on the other hand, is found to be different. MNDO calculations show that a torsion angle of 41.2° is 2.2 kcal mol^{-1} more stable than the planar $(CO)_2$ chromophore. MMP1[50] also calculated a distorted $(CO)_2$ chromophore with $\Theta_{CO/CO} = 45.7°$.

MNDO optimization based on the MMP1 geometry as a starting point results in a local minimum with $\Theta_{CO/CO} = 41.2°$, whilst optimization using X-ray structure results in a minimum of similar energies with $\Theta_{CO/CO} = 0.3°$.

The HAM/3 model is suited to associate these geometrical differences with orbital energy changes. Calculated orbital

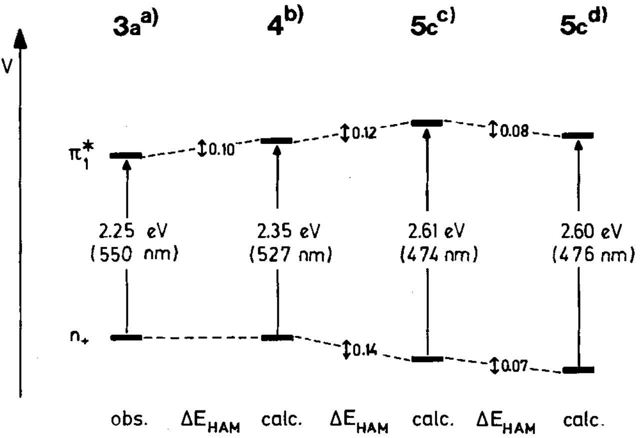


Figure 5. Relationship between experimental transition energies and calculated HAM orbital energies. Geometry is MNDO optimized (see text): $\Theta_{CO/CO}$ a) 1°, b) 39°, c) 41.2°, d) 0.3°

energy changes for n_+ and π^*_1 are given in Figure 5 as correction factors for the observed transition energies of the five-membered ring trione **3a**. These HAM orbital energy changes can be considered directly as changes in the transition energy[30]. Thus it can be shown that the hypsochromic shift from **3a** to **4** is due to a π^* destabilization and that the further hypsochromic shift from **4** to **5c** is due to an n_+ stabilization. The latter is also experimentally observed (Table 9). It appears to be unimportant which conformer of **5c** is used in the HAM calculation.

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Experimental

In the descriptive section of this study general carotinoid nomenclature is used whilst IUPAC nomenclature is to be found in the experimental part.

Apparatus and materials: ^1H NMR: 60 MHz Varian EM 360, 80 MHz Bruker WP 80. – ^{13}C NMR: 25.2 MHz Varian XL 100. – UV: Zeiss DMR 21 114 Q III. – IR: Perkin-Elmer Grating spectrometer 297, Perkin-Elmer spectrometer 710 B. – PE: Leybold-Heraeus spectrometer UPG 200. – MS: Varian MAT CH-5. – GC: Hewlett-Packard 5840 A with integrator; column material: 10% UCC W 982 on Chromosorb W AW 80. – TLC: TLC Aluminium foil plates silica gel 60 F_{254} (Merck). – CLC: Silica gel MN 60, 70–220 Mesh (Macherey and Nagel). – Melting points (uncorrected): Büchi SMD 20. – Elemental analyses: Institut für Pharmazeutische Chemie der Univ. Düsseldorf.

The synthesis of starting materials and comparison with substances obtained via other routes was achieved according to the literature: 2,4,4-trimethyl-2-cyclopenten-1-one (**6a**), 2,4,4-trimethyl-3-(nitromethyl)cyclopentanone (**7a**), 2,2,5-trimethyl-4-oxocyclopentanecarbaldehyde (**8a**), 2,5,5-trimethyl-3-oxo-1-cyclopentene-1-carbaldehyde (**9a**), and 2,4,4-trimethyl-3-(*trans*-3-oxo-1-butenyl)-2-cyclopenten-1-one (**10a**) according to ref.[5]; 4,4-dimethyl-2-cyclopenten-1-one (**6b**) according to ref.[52]; 3-ethoxy-5,5-dimethyl-2-cyclohexen-1-one (**19**) and 5,5-dimethyl-2-cyclohexen-1-one (**20a**) according to ref.[53]; 5,5-dimethyl-3-phenyl-2-cyclohexen-1-one (**20b**) according to ref.[54]; 5,5-dimethyl-3-vinyl-2-cyclohexen-1-one (**20d**) according to ref.[55]; 3,3-dimethyl-5-oxocyclohexanecarbaldehyde (**22**) and 5,5-dimethyl-3-oxo-1-cyclohexene-1-carbaldehyde (**25**) according to ref.[56]; 6-hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one (**24c**) according to ref.[57]; 2,6,6-trimethyl-2-cyclohexene-1,4-dione (**26**) according to ref.[8,58]; 2-methyl-2-cyclohexen-1-one for the preparation of **32** according to ref.[59]; 2,5,5-trimethyl-3-oxo-1-cyclopentene-1-carboxylic acid according to ref.[60]; (2-oxopropylidene)triphenylphosphorane according to ref.[61]; ethyl (diethoxyphosphoryl)acetate for the preparation of **14a** according to ref.[62]; 2,4,4-trimethyl-3-(*trans*-3-oxo-1-butenyl)-2-cyclohexen-1-one (**30**) according to ref.[63].

A: *Synthesis of the Nitromethane Adducts* **7b**, **21**, *and 2-Methyl-3-(nitromethyl)cyclohexanone:* The cycloalkenone is stirred with 5 equivalent weights of dried nitromethane and several ml of Triton B at 70–80°C (GC control). The solution is then cooled, poured into ice-cold 1 N H_2SO_4 and extracted several times with ether. After drying with $MgSO_4$, the solvent is removed and the residue is either distilled in vacuo or recrystallized.

B: *Synthesis of the Saturated Aldehydes* **8b**, **22**, *and 2-Methyl-3-oxocyclohexanecarbaldehyde:* The solution of the nitromethane adduct in 90% methanol is mixed with 1 equivalent of NaOH. The mixture is cooled to −60 to −70°C and treated with ca. 1.2 equivalents of ozone. Excess ozone is removed with N_2 and 2 equivalents of dimethyl sulfide is added to the cold solution. The mixture is allowed to reach room temperature and is then evaporated. The residue is extracted several times with ether, the combined ether layers are washed with a 10% $Na_2S_2O_3$ solution and then dried with $MgSO_4$. The ether is evaporated and the residue is distilled in vacuo.

C: *Synthesis of the Unsaturated Aldehydes* **9b**, **15a**, **25** *and 2-Methyl-3-oxo-1-cyclohexene-1-carbaldehyde:* A suspension of the saturated compound is stirred with 0.9 equivalents of dichlorodicyanoquinone and a catalytic amount of *p*-toluenesulfonic acid in absol. toluene at 80–100°C under nitrogen. The reaction is complete when the colour has changed from red to light yellow. The mixture is cooled to 0°C, and after removal of the precipitated hydroquinone it is filtered over neutral aluminium oxide. The solvent is evaporated and the mixture is distilled in vacuo.

D: *Synthesis of* **10b**, **31**, *and* **32** *via Wittig Reaction:* A solution of the unsaturated aldehyde in dry chloroform is stirred with 2 equivalents of (2-oxopropylidene)triphenylphosphorane[61] at room temperature. The solvent is evaporated and after addition of little petroleum ether triphenylphosphane oxide is removed by filtration. After removal of the ether the residue is distilled in vacuo or recrystallized.

E: *Synthesis of* **3a**, **4**, **5b**, **5c**, **11a**, **11b**, **16a**, **17a**, *and* **18a** *via Selenium Dioxide Oxidation:* To a solution of the starting material in the given solvent (Table 11) 0.9 equivalents of SeO_2 are added. The suspension is then heated under reflux for several hours and whilst still hot the precipitated selenium is removed. After removal of the solvent the residue is sublimed in vacuo or recrystallized.

2,4,4-Trimethyl-3-vinylcyclopentanone (**12a**): 20.1 g (50 mmol) of methyltriphenylphosphonium iodide is placed in a 250 ml flask fitted with reflux condenser, dropping funnel, and gas inlet. The flask is evacuated and then filled with dry nitrogen. 100 ml of dry tetrahydrofuran is added against a nitrogen current and then 30.8 ml of a 15% *n*-butyllithium solution in *n*-hexane is added. The solution is stirred for 30 min at room temperature and after cooling in ice, a solution of 7.6 g (50 mmol) of **8a** in 30 ml of dry tetrahydrofuran is added dropwise. After a further 1.5 h stirring at room temperature, the solvent is removed and the residue then extracted several times with petroleum ether. The combined organic layers are filtered, washed with water, and dried with $MgSO_4$. After removal of the ether the residue is distilled in vacuo (Table 11).

Ethyl 2,5,5-Trimethyl-3-oxo-1-cyclopentene-1-carboxylate (**13a**): A mixture of 5.0 g (29 mmol) of 2,5,5-trimethyl-3-oxo-1-cyclopentene-1-carboxylic acid, 4.0 g (86 mmol) of ethanol, and 1.5 g of concentrated sulfuric acid in 50 ml of $CHCl_3$ is heated for 4 h with continual removal of water. After cooling, the organic layer is washed with water, 5% $NaHCO_3$ solution, and then several times with water. The layer is dried with Na_2SO_4, the solvent removed, and the residue is distilled in vacuo.

Ethyl 3-(2,5,5-Trimethyl-3-oxo-1-cyclopenten-1-yl)propenoate (**14a**): 0.49 g (26 mmol) of sodium hydride (80% in paraffin oil) is added to 60 ml of dry tetrahydrofuran under nitrogen in a 500 ml flask fitted with reflux condenser, dropping funnel, and nitrogen inlet. 5.8 g (26 mmol) of ethyl (diethoxyphosphoryl)acetate is added slowly at 0°C, after which the mixture is stirred at room temperature until no further hydrogen evolution is observed. After cooling to 0°C, 4.0 g (26 mmol) of **9a** in dry tetrahydrofuran is added and the mixture is then stirred for a further 3 h at room temperature.

Table 11. Physical and analytical data of the prepared compounds

No	Name	B. p. (Yield %)	M. p. (Solvent)	Properties	Empirical formula (Molar mass)	Analysis				Remarks
							C	H	N	
3a	2,5,5-Trimethyl-3,4-dioxo-1-cyclopentene-1-carbaldehyde	– (62)	68 (Ether)	Ruby crystals	$C_9H_{10}O_3$ (166.2)	Calcd. Found	65.05 65.06	6.07 6.02		Solvent: gl. acetic acid. Chromatographed on short silica column. Eluent CH_2Cl_2. Recrystallized from ether
4	5,5-Dimethyl-3,4-dioxo-1-cyclohexene-1-carbaldehyde	– (63)	86 (Ether)	Yellow needles	$C_9H_{10}O_3$ (166.2)	Calcd. Found	65.05 64.81	6.07 5.96		Solvent: gl. acetic acid. Recryst. from ether
5b	3,3-Dimethyl-5-phenyl-5-cyclohexene-1,2,4-trione	– (20)	158 (Ether)	Yellow crystals	$C_{14}H_{12}O_3$ (228.25)	Calcd. Found	73.67 73.48	5.30 5.04		Solvent: gl. acetic acid. Recryst. from ether
5c	3,3,5-Trimethyl-5-cyclohexene-1,2,4-trione	– (28)	89 (Ether)	Yellow crystals	$C_9H_{10}O_3$ (166.2)	Calcd. Found	65.05 64.94	6.07 6.11		Solvent: Dioxane/H_2O (17:1). Recryst. from ether
7b	3,3-Dimethyl-4-(nitromethyl)cyclopentanone	95/0.07 Torr (80)	–	Colourless wax	$C_8H_{13}NO_3$ (171.2)	Calcd. Found	56.13 56.11	7.65 7.63	8.18 8.21	–
8b	2,2-Dimethyl-4-oxocyclopentanecarbaldehyde	63/0.1 Torr (53)	–	Colourless crystals	$C_8H_{12}O_2$ (140.2)	Calcd. Found Dimedone Derivative	71.61 71.59	8.52 8.46		–
9b	5,5-Dimethyl-3-oxo-1-cyclopentene-1-carbaldehyde	50/0.1 Torr (50)	–	Yellow crystals	$C_8H_{10}O_2$ (138.2)	Calcd. Found	69.54 69.70	7.30 7.33		–
10b	4,4-Dimethyl-3-(*trans*-3-oxo-1-butenyl)-2-cyclopenten-1-one	105/0.15 Torr (51)	–	Yellow crystals	$C_{11}H_{14}O_2$ (178.2)	Calcd. Found	74.13 74.13	7.92 7.92		–
11a	3,5,5-Trimethyl-3-cyclopentene-1,2-dione	– (37)	102 (Ether)	Yellow crystals	$C_8H_{10}O_2$ (138.2)	Calcd. Found	69.54 69.37	7.30 7.21		Solvent: gl. acetic acid. Sublimation at 50°C/0.05 Torr
11b	5,5-Dimethyl-3-cyclopentene-1,2-dione	– (17)	25 (Ether)	Orange wax	$C_7H_8O_2$ (124.1)	Calcd. Found	67.73 68.06	6.50 6.55		Solvent: Dioxane. Sublimation at 30°C/0.05 Torr
12a	2,4,4-Trimethyl-3-vinylcyclopentanone	50/4.5 Torr (35)	–	Colourless liquid	$C_{10}H_{16}O$ (152.2)	Calcd. Found	57.83 57.56	6.02 6.04	16.86 16.88	–
13a	Ethyl 2,5,5-trimethyl-3-oxo-1-cyclopentene-1-carboxylate	52/0.05 Torr (49)	–	Colourless liquid	$C_{11}H_{16}O_3$ (196.25)	Calcd. Found Derivative: 2,4-Dinitrophenylhydrazone	54.25 54.26	5.36 5.40	14.45 14.45	–
14a	Ethyl 3-(2,5,5-trimethyl-3-oxo-1-cyclopenten-1-yl)propenoate	– (49)	68 (Ether)	Colourless crystals	$C_{13}H_{18}O_3$ (222.3)	Calcd. Found	70.24 70.35	8.16 8.16		–
15a	2,4,4-Trimethyl-3-vinyl-2-cyclopenten-1-one	35/1 Torr (35)	–	Colourless liquid	$C_{10}H_{14}O$ (150.2)	Calcd. Found Derivative: 2,4-Dinitrophenylhydrazone	58.17 58.13	5.45 5.40	16.96 17.00	–
16a	3,5,5-Trimethyl-4-vinyl-3-cyclopentene-1,2-dione	– (38)	98 (Ether)	Orange crystals	$C_{10}H_{12}O_2$ (164.2)	Calcd. Found	73.10 72.96	7.31 7.37		Solvent: gl. acetic acid. Sublimation at 60°C/0.05 Torr
17a	Ethyl 2,5,5-trimethyl-3,4-dioxo-1-cyclopentene-1-carboxylate	– (56)	31 (Ether)	Red crystals	$C_{11}H_{14}O_4$ (210.2)	Calcd. Found	62.85 62.30	6.71 6.65		Solvent: Dioxane. Chromatographed on short silica column. Eluent CH_2Cl_2. Recryst. from ether
18a	Ethyl 3-(2,5,5-trimethyl-3,4-dioxo-1-cyclopenten-1-yl)-propenoate	– (61)	112 (Ether)	Red crystals	$C_{13}H_{16}O_4$ (236.3)	Calcd. Found	66.08 65.97	6.83 6.97		Solvent: Dioxane. Recryst. from ether
21	3,3-Dimethyl-5-(nitromethyl)cyclohexanone	100–103/0.01 Torr (50)	46 (Ether)	Colourless crystals	$C_9H_{15}NO_3$ (185.2)	Calcd. Found	58.36 57.80	8.16 8.25	7.56 7.40	Recryst. from methanol
23a	6-Acetoxy-5,5-dimethyl-2-cyclohexen-1-one	– (55)	96 (Ethyl acetate)	Colourless crystals	$C_{10}H_{14}O_3$ (182.2)	Calcd. Found	65.91 65.81	7.74 8.04		6 h reflux
23b	6-Acetoxy-5,5-dimethyl-3-phenyl-2-cyclohexen-1-one	– (30)	89 (Ethyl acetate)	Colourless crystals	$C_{16}H_{18}O_3$ (258.3)	Calcd. Found	74.39 74.19	7.02 7.20		15 h reflux
24a	6-Hydroxy-5,5-dimethyl-2-cyclohexen-1-one	104–105/15 Torr (55)	35 (Ethyl acetate)	Colourless crystals	$C_8H_{12}O_2$ (140.2)	Calcd. Found	68.54 67.45	8.63 8.60		–

Table 11 (*continued*)

No	Name	B. p. (Yield %)	M. p. (Solvent)	Properties	Empirical formula (Molar mass)	Analysis				Remarks
							C	H	N	
24b	6-Hydroxy-5,5-dimethyl-3-phenyl-2-cyclohexen-1-one	– (88)	85 (Ethyl acetate)	Colourless crystals	$C_{14}H_{16}O_2$ (216.2)	Calcd. Found	77.75 77.83	7.46 7.34		–
26c	2,6,6-Trimethyl-2-cyclohexene-1,4-dione	– (56)	21 (Hexane)	Colourless crystals	$C_9H_{12}O_2$ (152.2)	–				–
27b	2-Hydroxy-6,6-dimethyl-4-phenyl-2,4-cyclohexadien-1-one	155/0.05 Torr (10)	123–124 (Ether)	Light yellow crystals	$C_{14}H_{14}O_2$ (214.3)	Calcd. Found	78.48 78.12	6.59 6.83		Kugelrohr distillation
28a	6,6-Dimethyl-3-cyclohexene-1,2-dione	– (40)	59–60 (Ether)	Yellow crystals	$C_8H_{10}O_2$ (138.2)	Calcd. Found	69.54 69.25	7.30 7.30		Sublimation at 70°C/15 Torr
28b	6,6-Dimethyl-4-phenyl-3-cyclohexene-1,2-dione	– (31)	81–82 (Ether)	Yellow crystals	$C_{14}H_{14}O_2$ (214.3)	Calcd. Found	78.48 78.41	6.59 6.62		Recryst. from ether at −70°C
28c	4,6,6-Trimethyl-3-cyclohexene-1,2-dione	– (32)	51 (Ether)	Yellow crystals	$C_9H_{12}O_2$ (152.2)	Calcd. Found	71.03 69.89	7.95 7.85		Sublimation at 70°C/15 Torr
31	4,4-Dimethyl-3-(*trans*-3-oxo-1-butenyl)-2-cyclohexen-1-one	– (60)	57 (Hexane)	Colourless crystals	$C_{12}H_{16}O_2$ (192.3)	Calcd. Found	74.97 74.85	8.39 8.43		Sublimation at 70°C/0.04 Torr
32	2-Methyl-3-(*trans*-3-oxo-1-butenyl)-2-cyclohexen-1-one	140/0.01 Torr (60)	–	Light yellow liquid	$C_{11}H_{14}O_2$ (178.2)	Calcd. Found	74.13 73.88	7.92 7.76		Kugelrohr distillation
	2-Methyl-3-(nitromethyl)cyclohexanone	78–80/0.03 Torr (80)	–	Colourless liquid	$C_8H_{13}NO_3$ (171.2)	Calcd. Found	56.13 56.32	7.65 7.68	8.18 8.20	–
	2-Methyl-3-oxocyclohexanecarbaldehyde	54/0.2 Torr (40)	–	Colourless liquid	$C_8H_{12}O_2$ (140.2)	Calcd. Found Dimedone Derivative	71.61 71.62	8.52 8.50		Extremly volatile
	2-Methyl-3-oxo-1-cyclohexene-1-carbaldehyde	55–58/0.3 Torr (60)	–	Light yellow liquid	$C_8H_{10}O_2$ (138.2)	Calcd. Found Derivative: Bis(dinitrophenylhydrazone)	48.20 47.96	3.64 3.92	22.48 22.41	Extremly volatile

After addition of 300 ml of water the mixture is extracted with ether. The organic layers are dried with Na_2SO_4, the ether is removed and the product is recrystallized from ether.

6-Acetoxy-5,5-dimethyl-2-cyclohexen-1-one (**23a**) *and 6-Acetoxy-5,5-dimethyl-3-phenyl-2-cyclohexen-1-one* (**23b**): 53.2 g (0.12 mol) of lead tetraacetate is suspended in a solution of 0.10 mol of **20a** or **20b** in 150 ml of dry toluene and heated for the given time (Table 11) under reflux. The mixture is then filtered and the filtrate is washed with water. The aqueous layer is extracted with ether, and after drying the organic layers with $MgSO_4$ the solvent is removed. The residue is recrystallized from ethyl acetate.

6-Hydroxy-5,5-dimethyl-2-cyclohexen-1-one (**24a**) *and 6-Hydroxy-5,5-dimethyl-3-phenyl-2-cyclohexen-1-one* (**24b**): 39 ml of 1 N NaOH is added to a solution of 30 mmol of **23a** or **23b** in 150 ml methanol under nitrogen at 0°C. The mixture is stirred for 2 h at room temperature, neutralized with 1 N HCl, and poured into 130 ml of ice-cold water. This is then extracted with ether. The ether layers are washed with brine and then dried with $MgSO_4$. The solvent is removed and the residue is distilled in vacuo. The resulting oil is then recrystallized from ethyl acetate.

5,5-Dimethyl-3-oxo-1-cyclohexene-1-carbaldehyde (**25**) (Alternative Method): 1 equivalent of ozone is led into a solution of 18.4 g (0.12 mol) of **20d** in 200 ml of CH_2Cl_2 at −78°C. Excess ozone is removed by a stream of nitrogen. 12.9 ml (0.14 mol) of dimethyl sulfide is then added at the same temperature. The mixture is left to stand for 12 h. The solvent is removed and the residue distilled in vacuo.

2,6,6-Trimethyl-2-cyclohexene-1,4-dione (**26c**): In a 1 l flask fitted with gas inlet, thermometer, and a 20 cm filled-column plus condenser a mixture of 300 g (2.17 mol) of isophorone, 9.64 g of dodecamolybdatophosphoric acid, 1.21 g of $CuSO_4 \cdot 5\,H_2O$, 1.24 g of molybdenium(VI) oxide, and 300 ml of xylene is heated to 100°C whilst a stream of air is passed through. After 100 h the hot reaction mixture is injected portionwise (50 ml) into 4–5 l of boiling hexane. The solution is heated for further 30 min under reflux. The precipitate is removed and the filtrate is evaporated. The residue is then distilled in vacuo (85–105°C/14 Torr). The distillate solidifies at −18°C. The crystals are sucked and washed with a little cold hexane.

Synthesis of **27b** *and* **28a–c**: The acyloin **24a–c** (10 mmol) is stirred in a mixture of dry acetic anhydride (20 ml) and dry dimethyl sulfoxide (30 ml) for 24 h at room temperature. The reaction mixture is poured into 200 ml of ice-cold water and then extracted with ether. The combined ether layers are washed with 10% $NaHCO_3$ solution and with water, dried with $MgSO_4$ and then evaporated. Residual dimethyl sulfoxide is removed in vacuo (40°C/10^{-3} Torr). The resulting oil is once more recrystallized from ether. The product is finally sublimed in vacuo.

Table 12. Spectral data of the prepared compounds

Compound	IR (cm^{-1})	UV (solvent) λ_{max}(nm) ε_{max}	^{1}H-NMR ($CDCl_3$) (ppm)	^{13}C-NMR ($CDCl_3$) (ppm)	MS m/Z (rel. Int. in %)
3a	2980, 2770 1760, 1720 1670, 1605	550 19 ($CHCl_3$)	1.48 (s,6H), 2.25 (s,3H), 10.55 (s,1H)	8.1 (q,CH_3), 22.1 (q,$(CH_3)_2$), 43.3 (s,C-5), 148.8 (s,C-2), 158 (s,C-1), 191.4 (d,CHO), 193.1 (s,C-3), 201.9 (s,C-4)	166 (70), 138 (72), 95 (68)
4	2930, 2900 2820, 1700 1660	474 30 (CH_3CN)	1.28 (s,6H), 2.76 (d,2H), 6.90 (t,1H), 9.85 (s,1H)	23.7 (q,CH_3), 36.3 (t,C-6), 46.9 (s,C-5), 137.5 (d,C-2), 153.1 (s,C-1), 185.5 (s,C-3), 192.8 (d,CHO), 197.9 (s,C-4)	166 (14), 138 (9), 110 (23), 95 (65), 81 (33), 70 (85)
5b	3050, 3000 2940, 1730 1670	452 89 ($CHCl_3$)	1.60 (s,6H), 7.40 (s,1H), 7.60 (s,5H)	21.4 (q,CH_3), 63.0 (s,C-3), 128.7 (d,C-meta), 129.0 (d,C-ortho), 131.3)d,C-para), 132.7 (s, C-ipso), 134.7 (d,C-6), 152.8 (s,C-5), 182.4 (s,C-1), 192.4 (s,C-2), 195.8 (s,C-4)	200 (47), 158 (14), 144 (12), 129 (26), 102 (100), 76 (15)
5c	2980, 2940 2870, 1730 1670	445 25 ($CHCl_3$)	1.45 (s,6H), 2.18 (d,3H), 7.08 (q,1H)	17.7 (q,CH_3), 21.5 (q,$(CH_3)_2$), 61.5 (s,C-3), 137.2 (d,C-6), 153.1 (s,C-5), 182.6 (s,C-1), 193.1 (s,C-2), 196.8 (s,C-4)	166 (40), 138 (32), 97 (100), 68 (85)
7b	2960, 1725 1540	–	1.10 (d,6H), 2.13 (s,2H), 2.45–3.00 (m,3H), 4.20–4.70 (m,2H)	21.7 (q,CH_3-cis), 27.0 (q,CH_3-trans), 38.1 (s, C-4), 41.0 (t,C-2), 44.0 (d,C-3), 54.4 (t,C-5), 76.4 (t,CH_2NO_2), 214.6 (s,C-1)	171 (31), 125 (7), 111 (6)
8b	2960, 1725	–	1.25 (d,6H), 2.20 (s,2H), 2.35–3.10 (m,3H), 9.90 (s,1H)	23.4 (q,CH_3-cis), 28.8 (q,CH_3-trans), 36.5 (t, C-2), 39.8 (s,C-5), 54.4 (t,C-4), 57.3 (d,C-1), 201.6 (d,CHO), 214.6 (s,C-3)	140 (30), 122 (5), 100 (80)
9b	3060, 2970 2820, 1720 1684	352 26 ($CHCl_3$)	1.10 (s,6H), 2.17 (s,2H), 6.30 (s,1H), 9.82 (s,1H)	26.8 (q,CH_3), 40.9 (s,C-5), 53.6 (t,C-4), 141.7 (d,C-2), 173.6 (s,C-1), 190.1 (d,CHO), 207.4 (s, C-3)	138 (80), 123 (18), 110 (45), 95 (100)
10b	2960, 1695	346 145 ($CHCl_3$)	1.34 (s,6H), 2.38 (s,3H), 2.43 (s,2H), 6.26 (s,1H), 6.70 (d,1H), 7.27 (d,1H)	27.2 (q,$C(\underline{C}H_3)_2$), 28.1 (q,C-4'), 42.0 (s,C-4), 52.2 (t,C-5), 129.8 (d,C-2), 133.1 (d,C-1'), 134.1 (d,C-2'), 176.8 (s,C-3), 196.8 (s,C-3'), 206.3 (s,C-1)	182 (15), 167 (18)
11a	3015, 2970 1755, 1705	486 19 ($CHCl_3$)	1.23 (s,6H), 1.92 (s,3H), 7.48 (s,1H)	23.2 (q,$C(\underline{C}H_3)_2$), 11.2 (q,$=C-CH_3$), 42.4 (s,C-5), 143.5 (s,C-3), 164.0 (d,C-4), 189.6 (s,C-2), 203.6 (s,C-1)	138 (60), 110 (66), 82 (47)
11b	3040, 2980 1773, 1725	482 20 ($CHCl_3$)	1.30 (s,6H), 6.74 (d,1H), 7.90 (d,1H)	22.9 (q,CH_3), 43.5 (s,C-4), 134.7 (d,C-3), 169.7 (d,C-4), 188.9 (s,C-2), 202.3 (s,C-1)	124 (48), 96 (74), 71 (44)
12a	2960, 2870 1740, 1640	--	0.95 (s,3H), 1.03 (d,3H), 1.13 (s,3H), 1.80–2.50 (m,4H), 5.07–5.13 (d,1H), 5.70 (d,1H)	13.1 (q,CH_3), 22.6 (q,$\underline{C}(CH_3)_2$), 37.2 (s,C-4), 46.7 (d,C-2), 53.4 (t,C-5), 59.6 (d,C-3), 117.7 (t,$=\underline{C}H_2$), 135.9 (d,=CH–), 218.4 (s,C-1)	150 (55), 135 (100), 107 (93)
13a	2970, 2862 1705	243 6900 ($CHCl_3$)	1.39 (t,3H), 1.41 (s,6H), 1.98 (s,3H), 2.43 (s,2H), 4.42 (q, 2H)	9.8 (q,$=C-\underline{C}H_3$), 14.2 (q,$-CH_2-\underline{C}H_3$), 27.5 (q,$C(\underline{C}H_3)$), 40.3 (s,C-5), 51.6 (t,C-4), 60.8 (t,$-O-\underline{C}H_2-$), 143.5 (s,C-2), 162.3 (s,C-1), 165.3 (s,–COO–), 207.6 (s,C-3)	--
14a	2980–2820, 1700	342 79 ($CHCl_3$)	1.38 (s,6H), 1.40 (t,3H), 1.88 (s,3H), 2.41 (s,2H), 4.34 (q, 2H), 6.35 (d,1H), 7.57 (d,1H)	9.2 (q,$=C-\underline{C}H_3$), 14.2 (q,$-CH_2-\underline{C}H_3$), 27.7 (q,$C(\underline{C}H_3)_2$), 40.5 (s,C-5'), 51.5 (t,C-4'), 60.8 (t,$-O-\underline{C}H_2-$), 126.3 (d,C-2), 135.6 (d,C-3), 139.6 (s,C-2'), 165.6 (s,C-1), 167.2 (s,C-1'), 206.7 (s,C-3')	222 (43), 207 (33), 194 (17), 149 (39)
15a	2960, 1695 1585	--	1.23 (s,6H), 1.78 (s,3H), 2.29 (s,2H), 5.65 (m,2H), 6.53 (d,1H)	9.0 (q,CH_3), 27.8 (q,$C(\underline{C}H_3)_2$), 40.4 (s,C-4), 51.4 (t,C-5), 123.6 (t,$=CH_2$), 129.3 (d,–CH=), 135.3 (s,C-2), 171.7 (s,C-3), 207.4 (s,C-1)	150 (94), 135 (100), 107 (94)
16a	3100, 2970 1755, 1690 1600	494 28 ($CHCl_3$)	1.37 (s,6H), 2.06 (s,3H), 5.97 (d,1H), 6.05 (d,1H), 6.83 (d,1H)	9.1 (CH_3), 22.6 (q,$C(\underline{C}H_3)_2$), 44.3 (s,C-5), 128.0 (t,$=\underline{C}H_2$), 128.7 (d,$-\underline{C}H=$), 140.4 (s,C-3), 168.0 (s, C-4), 188.7 (s,C-2), 203.2 (s,C-1)	164 (31), 136 (52), 121 (46)
17a	2970, 2930 1760, 1708	510 23 ($CHCl_3$)	1.41 (s,6H), 1.43 (t,3H), 2.13 (s,3H), 4.37 (q,2H), 6.61 (d,1H), 7.75 (d,1H)	10.4 (q,CH_3), 14.2 (q,$CH_2-\underline{C}H_3$), 22.5 (q,$C(\underline{C}H_3)_2$), 44.4 (s,C-5), 61.7 (t,$-O-\underline{C}H_2-$), 146.3 (s,C-2), 158.6 (s,C-1), 164.6 (s,$-\underline{C}OO-$), 190.5 (s,C-3), 201.9 (s,C-4)	210 (37), 182 (42), 154 (81)
18a	2980–2870, 1760, 1690, 1180	513 42 ($CHCl_3$)	1.40 (t,3H), 1.42 (s,6H), 2.11 (q,2H), 6.61 (d,1H), 7.75 (d,1H)	9.4 (q,CH_3), 14.2 (q,$CH_2-\underline{C}H_3$), 22.5 (q,$C(\underline{C}H_3)_2$), 44.3 (s,C-5'), 61.3 (t,$-O-\underline{C}H_2-$), 129.3 (d,C-2), 134.7 (d,C-3), 143.7 (s,C-2'), 164.3 (s,C-1'), 165.0 (s,C-1), 188.7 (s,C-3'), 202.9 (s,C-4')	236 (41), 208 (22), 180 (39)
21	2950, 2860 1710, 1540 1380	--	0.95 (s,3H), 1.15 (s,3H), 1.30 (m,7H), 4.40 (d,2H)	25.4 (q,CH_3-cis), 31.7 (q,CH_3-trans), 33.3 (d,C-3), 34.6 (s,C-5), 41.3 (t,C-4), 43.5 (t,C-2), 53.9 (t, C-6), 78.5 (t,CH_2NO_2), 207.9 (s.C-1)	185 (14), 170 (14), 139 (63), 110 (64), 83 (100)

Table 12 (*continued*)

Compound	IR (cm^{-1})	UV (solvent) λ_{max}(nm) ε_{max}	^{1}H-NMR ($CDCl_3$) (ppm)	^{13}C-NMR ($CDCl_3$) (ppm)	MS m/Z (rel. Int. in %)
23a	3040, 2960 2900, 1725 1680	--	1.00 (s,3H), 1.15 (s,3H), 2.20 (s,3H), 2.45 (m,2H), 5.20 (s,1H), 6.00 (d,1H), 6.80 (d,1H)	19.7 (q,CH_3-cis), 20.5 (q,$\underline{C}H_3$CO), 27.1 (q,CH_3-trans), 38.2 (s,C-5), 40.8 (t,C-4), 80.9 (d,C-6), 127.8 (d,C-2), 146.4 (d,C-3), 169.8 (s,$\underline{C}$=O), 193.1 (s,C-1)	182 (9), 140 (17), 122 (36), 114 (89)
23b	3050, 2950, 1735, 1670	--	1.05 (s,3H), 1.20 (s,3H), 2.25 (s,3H), 2.80–2.95 (m,2H), 5.40 (s,1H), 7.25–7.70 (m,5H)	19.8 (q,CH_3-cis), 20.6 (q,$\underline{C}H_3$CO), 27.4 (q,CH_3-trans), 37.8 (s,C-5), 43.0 (t,C-4), 80.5 (d,C-6), 123.0 (d,C-2), 126.0 (d,C-ortho), 128.6 (d,C-meta), 130.1 (d,C-para), 137.9 (s,C-ipso), 156.3 (s,C-3), 170.1 (s,C=O), 193.1 (s,C-1)	258 (18), 216 (8), 198 (16), 170 (19), 144 (100), 116 (27)
24a	3450, 2970, 2930, 1670	--	0.80 (s,3H), 1.15 (s,3H), 2.35 (m,2H), 3.65 (s,1H), 4.00 (s,1H), 6.05 (d,1H), 6.95 (m,1H)	18.0 (q,CH_3-cis), 27.6 (q,CH_3-trans), 40.1 (s,C-5), 40.7 (t,C-4), 80.4 (d,C-6), 126.4 (d,C-2), 149.3 (d,C-3), 199.9 (s,C-1)	140 (10), 92 (17), 79 (28), 72 (100)
24b	3370, 3050, 2950, 1660	--	0.95 (s,3H), 1.35 (s,3H), 2.80 (s,2H), 3.80 (s,1H), 4.15 (s,1H), 6.55 (d,1H), 7.35–7.80 (m,5H)	18.0 (q,CH_3-cis), 27.8 (q,CH_3-trans), 39.7 (s,C-5), 42.7 (t,C-4), 79.9 (d,C-6), 121.4 (d,C-2), 126.0 (d,C-ortho), 128.6 (d,C-meta), 130.1 (d,C-para), 138.0 (s,C-ipso), 158.2 (s,C-3), 199.5 (s,C-1)	216 (25), 188 (9), 173 (9), 145 (60), 144 (100), 117 (18), 116 (55)
26c	2980, 2930, 2870, 1680, 1620	368 28 (CH_3CN)	1.25 (s,6H), 2.02 (d,3H), 2.73 (s,2H), 6.57 (q,1H)	16.7 (q,CH_3), 26.0 (q,C($\underline{C}H_3)_2$), 45.0 (s,C-6), 51.7 (t,C-5), 136.8 (d,C-3), 148.5 (s,C-2), 197.1 (s,C-4), 202.8 (s,C-1)	--
27b	3380, 3060, 3020, 2970, 1635	352 1740 (CH_3Cl)	1.35 (s,6H), 5.90 (d,1H), 6.25 (s,1H), 6.66 (d,1H), 7.30–7.70 (m,5H)	25.8 (q,CH_3), 46.3 (s,C-6), 115.5 (d,C-3), 125.6 d,C-ortho), 127.5 (d,C-para), 128.5 (d,C-meta), 130.7 (s,C-ipso*), 134.9 (d,C-5), 139.1 (s,C-4*), 146.3 (s,C-2), 201.2 (s,C-1) * assignment uncertain	214 (100), 199 (48), 186 (96), 171 (96), 144 (46)
28a	3020, 2980, 2940, 1735, 1690	431 25 (CH_3CN)	1.30 (s,6H), 2.75 (dd,2H), 6.45 (dt,1H), 7.20 (dt,1H)	24.0 (q,CH_3), 41.7 (t,C-5), 48.3 (s,C-6), 130.6 (d,C-3), 151.6 (d,C-4), 184.3 (s,C-2), 199.8 (s,C-1)	138 (16), 123 (3), 110 (14), 95 (100), 67 (70)
28b	3060, 3040, 2980, 2950, 1725, 1660	442 76 (CH_3CN)	1.35 (s,6H), 3:10 (s,2H), 6.75 (s,1H), 7.30 (m,5H)	24.2 (q,CH_3), 43.4 (t,C-5), 47.3 (s,C-6), 125.8 (d,C-3), 126.2, 128.9 (d,C-meta, C-ortho), 131.0 d,C-para), 137.7 (s,C-ipso), 160.6 (s,C-4), 183.5 (s,C-2), 199.6 (s,C-1)	214 (3), 186 (59), 171 (100), 144 (33), 128 (25), 115 (32)
28c	2970, 2930, 1715, 1660	425 20 (CH_3CN)	1,25 (s,6H), 2.10 (s,3H), 2.65 (s,2H), 6.30 (m,1H)	24.0 (q,C($\underline{C}H_3)_2$), 25.2 (q,CH_3), 46.3 (s,C-6), 46.8 (t,C-5), 127.6 (d,C-3), 165.2 (s,C-4), 183.0 (s,C-2), 200.0 (s,C-1)	152(3), 124(13), 109 (100), 82(71), 81(52)
31	2970, 2940, 1670	--	1.20 (s,6H), 1.90 (m,2H), 2.30 (s,3H), 2.40 (m,2H), 6.10 (s,1H), 6.55 (d,1H), 7.40 (d,1H)	26.7 (q,C($\underline{C}H_3)_2$), 28.4 (q,C-4'), 34.3 (t,C-6), 34.7 (s,C-4), 37.4 (t,C-5), 125.1 (d,C-2), 131.3 (d,C-2'), 139.2 (d,C-1'), 162.9 (s,C-3) 196.9 (s,C-3'),.198.6 (s,C-1)	192 (86), 177 (20), 150 (28), 149 (50), 122 (100), 107 (28)
32	2940, 1712, 1672	298 6480 ($CHCl_3$)	2.05 (s,2H), 2.42 (s,6H), 2.55 (s,4H), 6.54 (d,1H), 7.78 (d,1H)	11.0 (q,$\underline{C}H_3$), 21.8 (t,C-5), 26.0 (t,C-4), 27.9 (q,C-4'), 37.7 (t,C-6), 131.1 (d,C-2'), 137.6 (s,C-2), 139.6 (d,C-1'), 146.6 (s,C-3), 197.5 (s,C-3'), 198.7 (s,C-1)	178 (22), 137 (28), 106 (33), 93 (27)
a)	2945, 1713, 1552	--	1.10 (d,3H), 1.50–2.60 (m,8H), 4.30–4.70 (m,2H)	11.4 (q,CH_3-cis), 11.7 (q,$\underline{C}H_3$-trans), 23.2 (t,C-5), 25.4 (t,C-4), 39.4 (t,C-6), 41.1 (d,C-2), 46.4 (d,C-3), 79.2 (t,$\underline{C}H_2NO_2$), 209.6 (s,C-1)	171 (15), 124 (26), 109 (29), 95 (37), 81 (40)
b)	2940, 1710,	--	1.10 (d,3H), 1.50–2.90 (m,8H), 9.62 (d,1H)	12.4 (q,CH_3-cis), 12.7 (q,CH_3-trans), 25.3 (t,C-5), 25.5 (t,C-4), 40.8 (t,C-6), 43.7 (d,C-2), 57.5 (d,C-3), 201.0 (d,$\underline{C}$HO), 210.1 (s,C-1)	--
c)	3160, 2960, 1740, 1710, 1678	244 853 ($CHCl_3$)	2.20 (s,3H), 1.80–2.80 (m,6H), 10.35 (s,1H)	9.3 (q,CH_3), 21.6 (t,C-5), 22.7 (t,C-4), 38.2 (t,C-6), 143.4 (s,C-2), 146.1 (s,C-3), 193.4 (d,$\underline{C}$HO), 200.9 (s,C-1)	--

[a] 2-Methyl-3-(nitromethyl)cyclohexanone. – [b] 2-Methyl-3-oxocyclohexanecarbaldehyde. – [c] 2-Methyl-3-oxo-1-cyclohexene-1-carbaldehyde.

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[1] *Small and Medium Rings*, Part 65; Part 64; K. Hassenrück, H. Höchstetter, H. D. Martin, A. Steigel, H. P. Wingen, *Chem. Ber.* **120** (1987) 203.

[2] [2a] M. B. Rubin, *Chem. Rev.* **75**, (1975) 177. – [2b] P. Bischof, R. Gleiter, P. Hofmann, *Helv. Chim. Acta* **58** (1975) 2130. – [2c] E. Beck, P. Hofmann, A. Sieber, *Tetrahedron Lett.* **22** (1981) 4683. – [2d] R. Gleiter, W. Dobler, M. Eckert-Maksic, *Nouv. J. Chim.* **6** (1982) 123.

[3] [3a] S. Hertzberg, S. Liaaen-Jensen, C. R. Enzell, G. W. Francis, *Acta Chem. Scand.* **23** (1969) 3290. – [3b] P. Beyer, H. Kleinig, W. Meister, G. Englert, *Z. Naturforsch., Teil C*, **34** (1979) 179. – [3c] T. Anke, J. Bäuerle, S. Backeus, W. Steglich, private communication.

[4] A. J. Aasen, S. Liaaen-Jensen, *Acta Chem. Scand.* **20** (1966) 1970.

[5] F. Kienzle, R. M. Minder, *Helv. Chim. Acta* **59** (1976) 439.

[6] **11a** has also been synthesized from dichlorocyclopentanone: L. de Buyck, R. Verhe, N. de Kimpe, D. Courthyn, N. Schamp, *Bull. Chem. Soc. Chim. Belg.* **90** (1981) 837.

[7] M. L. Quesada, R. H. Schlessinger, *Synth. Commun.* **6** (1976) 555.

[8] Hoffmann La Roche, F. and Co., A.G. (Inv. M. Seuret, E. Widmer), D.O.S. 2526851 (8. Jan. 1976) [*Chem. Abstr.* **84** (1978) P164269e].

[9] F. Frickel in *The Retinoids* (M. B. Sporn, A. B. Roberts, D. S. Goodman, Ed.), Vol. 1, p. 7, Academic Press, London 1984.

[10] R. Rowan, A. Warshel, B. D. Sykes, M. Karplus, *Biochemistry* **13** (1974) 970; B. Honig, B. Hudson, B. D. Sykes, M. Karplus, *Proc. Nat. Acad. Sci. USA* **68** (1971) 1289; G. S. Harbison, S. O. Smith, J. A. Pardoen, J. M. L. Courtin, J. Lugtenburg, J. Herzfeld, R. A. Mathies, R. G. Griffin, *Biochemistry* **24** (1985) 6955; K. Müllen, H. Schmickler, B. Frei, H. R. Wolf, *Tetrahedron Lett.* **27** (1986) 477; R. S. H. Liu, J. P. Zingoni, A. Kini, M. Trammell, D. Chu, A. E. Asato, T. T. Bopp, *J. Org. Chem.* **48** (1983) 4817.

[11] A. Gieren, V. Lamm, D. Oesterhelt, H.-J. Schlude, *Z. Naturforsch., Teil B*, **37** (1982) 1612.

[12] B. Honig, A. Warshel, M. Karplus, *Acc. Chem. Res.* **8** (1975) 92.

[13] H. Schenk, *Acta Crystallogr., Sect. B*, **27** (1971) 667.

[14] G. Englert in *Carotenoids and Biochemistry* (G. Britton, T. W. Goodwin, Ed.), p. 107, Pergamon Press, Oxford 1982.

[15] K. G. K. Pachler, *J. Magn. Reson.* **7** (1972) 442.

[16] R. Aydin, J. P. Louse, H. Günther, *Angew. Chem.* **94** (1982) 451; *Angew. Chem. Int. Ed. Engl.* **21** (1982) 449; U. Vogeli, W. v. Philipsborn, *Org. Magn. Reson.* **7** (1975) 617.

[17] [17a] Investigations are under way to test this relationship for the fragment H–C–C=C. – [17b] C. A. Kingsbury, D. Draney, A. Sopchik, W. Rissler, D. Durham, *J. Org. Chem.* **41** (1976) 3863.

[18] N. L. Allinger, J. T. Sprague, *J. Am. Chem. Soc.* **95** (1973) 3893 (QCPE Nr. 318); N. L. Allinger, *ibid.* **99** (1977) 975.

[19] R. E. Schirmer, J. H. Noggle, J. P. Davis, P. A. Hart, *J. Am. Chem. Soc.* **92** (1970) 3266.

[20] Part of the *Thesis* of B. Middelhauve, Universität Düsseldorf 1986.

[21] J. Hocken, *Thesis*, Universität Düsseldorf 1984.

[22] D. Brodalla, D. Mootz, R. Boese, W. Osswald, *J. Appl. Cryst.* **18** (1985) 316.

[23] A. Simon, *J. Appl. Cryst.* **4** (1971) 138.

[24] *SHELXTL, Structure Determination Systems-Revision* **4**, Nicolet Analytical Instruments, Madison, WI, USA 1983.

[25] C. K. Johnson, *Program ORTEP II, ORNL-5138*, Oak Ridge National Laboratory, Oak Ridge, TN, USA 1976.

[26] Further details of the structure determination are deposited at Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (West Germany). These data are available with quotation of the registry number CSD 51990, the authors, and the reference to this publication.

[27] L. Tsai, J. V. Silverton, H. T. Ling, *J. Org. Chem.* **43** (1978) 4415.

[28] P. B. Hitchcock, R. W. McCabe, D. W. Young, G. M. Davies, *J. Chem. Soc., Chem. Commun.* **12** (1981) 608.

[29] S. J. A. Jansing, J. G. White, *J. Am. Chem. Soc.* **92** (1970) 7187.

[30] L. Asbrink, C. Fridh, E. Lindholm, *Chem. Phys. Lett.* **52** (1977) 69, 72; QCPE Nr. 393; E. Lindholm, L. Asbrink, *Molecular Orbitals and their Energies, Studied by the Semiempirical HAM Method*, Springer Verlag, Berlin 1985.

[31] R. C. Bingham, M. J. S. Dewar, D. H. Lo, *J. Am. Chem. Soc.* **97** (1975) 1285.

[32] M. J. S. Dewar, W. Thiel, *J. Am. Chem. Soc.* **99** (1977) 4899, 4907.

[33] G. Pfister-Guillouzo, S. Geribaldi, J. F. Gal, *Can. J. Chem.* **60** (1982) 1163.

[34] G. Hentrich, E. Gunkel, M. Klessinger, *J. Mol. Struct.* **21** (1974) 231.

[35] H. van Dam, A. Oskam, *J. Electron Spectrosc. Rel. Phenom.* **13** (1978) 273.

[36] G. Granozzi, D. Ajo, I. Fragala, *J. Electron Spectrosc. Rel. Phenom.* **18** (1980) 267.

[37] D. Dougherty, P. Brint, S. P. McGlynn, *J. Am. Chem. Soc.* **100** (1978) 5597.

[38] H. D. Martin, B. Mayer, *Angew. Chem.* **95** (1983) 281; *Angew. Chem. Int. Ed. Engl.* **22** (1983) 283.

[39] D. Dougherty, S. P. McGlynn, *J. Am. Chem. Soc.* **99** (1977) 3234.

[40] P. Jaques, J. Faure, O. Chalvet, H. H. Jaffé, *J. Phys. Chem.* **85** (1981) 473.

[41] L. Asbrink, G. Bieri, C. Fridh, E. Lindholm, D. P. Chong, *Chem. Phys.* **43** (1979) 189.

[42] R. Gleiter, G. Jähne, M. Oda, M. Jyoda, *J. Org. Chem.* **50** (1985) 678.

[43] A. Modelli, P. D. Burrow, *J. Phys. Chem.* **88** (1984) 3550; M. Guerra, D. Jones, G. Distefano, A. Modelli, *Chem. Phys.* **85** (1984) 389.

[44] G. Lauer, W. Schäfer, A. Schweig, *Chem. Phys. Lett.* **33** (1975) 312.

[45] J. Del Bene, H. H. Jaffé, *J. Chem. Phys.* **48** (1968) 1807.

[46] W. Hug, J. Kuhn, K. J. Seibold, H. Labhart, G. Wagnière, *Helv. Chim. Acta* **54** (1971) 1451.

[47] J. F. Arnett, G. Newkome, W. L. Mattice, S. P. McGlynn, *J. Am. Chem. Soc.* **96** (1974) 4385.

[48] N. J. Leonard, P. M. Mader, *J. Am. Chem. Soc.* **72** (1950) 5388.

[49] P. L. Verheijdt, H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2* **1982**, 1541.

[50] In addition to the parameters of MM 1[18] and of R. Isaksson, T. Liljefors, *J. Chem. Soc., Perkin Trans. 2*, **1983**, 1351, we used the following values: 3-3-2-2 (V_1 −0.93, V_2 15.0, V_3 0), 3-3-2-5 (V_1 0.4, V_2 9.82, V_3 0), 3-1-3-2 ($V_1 = V_2 = V_3 = 0$), 3-3-1-3 ($V_1 = V_2 = V_3 = 0$), 2-3-3-1 (V_1 0, V_2 1.0, V_3 0), 2-3-3-7 (V_1 0, V_2 1.0, V_3 0), [kcal mol^{-1}]; 3-3-1 (k_b 0.5, Θ°_{abc} 120.0), 3-3-2 (k_b 0.6, Θ°_{abc}116.0) [mdyn Å/rad^2]; bond moment 3-7 2.90 [D].

[51] The crystal data of six-membered ring diketones are to be published separately: B. Middelhauve, D. Mootz, H. D. Martin. Some relevant data of **5c** (3,3,5-Trimethyl-5-cyclohexene-1,2,4-trione) are given here: O1–C1–C2–O2 6.3°, C6–C1–C2–C3 10.9°, C1–C2–C3–C4 −33.9°, C2–C3–C4–C5 40.9°, C3–C4–C5–C6 −23.7°, C4–C5–C6–C1 −3.1°, C5–C6–C1–C2 9.4°. Bond lengths (pm): C1–C2 154.7, C1–C6 146.3, C5–C6 134.2.

[52] R. W. Holder, J. P. Daub, W. E. Baker, R. H. Gilbert III, N. A. Graf, *J. Org. Chem.* **47** (1982) 1445.

[53] R. L. Frank, H. K. Hall, *J. Am. Chem. Soc.* **72** (1950) 1645.

[54] G. F. Woods, *J. Am. Chem. Soc.* **69** (1947) 2549.

[55] C. Crisan, H. Normant, *Bull. Soc. Chim. Fr.* **1957**, 1451.

[56] G. de Weck, H. R. Wolf, *Helv. Chim. Acta* **64** (1981) 224.

[57] A. W. Fort, *J. Org. Chem.* **26** (1961) 332.

[58] V. J. Freer, P. Yates, *Chem. Lett.* **1984**, 2031.

[59] E. W. Warnhoff, D. G. Martin, W. S. Johnson, *Org. Synth.*, Coll. Vol. IV, p. 162.

[60] T. Wakui, Y. Otsuji, E. Imoto, *Bull. Chem. Soc. Jpn.* **47** (1974) 1522, 2267.

[61] F. Ramirez, S. Dershowitz, *J. Org. Chem.* **22** (1957) 41.

[62] J. Wolinsky, K. L. Erickson, *J. Org. Chem.* **30** (1965) 2208.

[63] E. Becher, R. Albrecht, K. Bernard, H. G. W. Leuenberger, H. Mayer, R. K. Müller, W. Schüep, H. P. Wagner, *Helv. Chim. Acta* **64** (1981) 2419.

[18/87]