

tuenten an C(2) zwar ein zu **b** analoges, aber wesentlich intensitätsschwächeres Ion bilden.

Im Spektrum von **2** erwähnenswert ist schliesslich noch das Ion der Masse 179, welches dem Verlust von HNC₂O und CH₃ aus dem Molekularion entspricht. – Verbindungen vom Typ **1**, die am Zentrum 2 einen alicyclischen Ring tragen, verhalten sich massenspektrometrisch völlig analog zu den bereits erwähnten Äthylenketalen von Steroidketonen.

Schliesslich sei noch darauf hingewiesen, dass in den Massenspektren von 1,3-Oxathiolanen mit gleichen Substituenten wie in **1** neben dem stets intensiveren Ion **b** auch das entsprechende Thioanalogon registriert wird.

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68. The Conformation and Chirality of α -Diketones

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(10. II. 72)

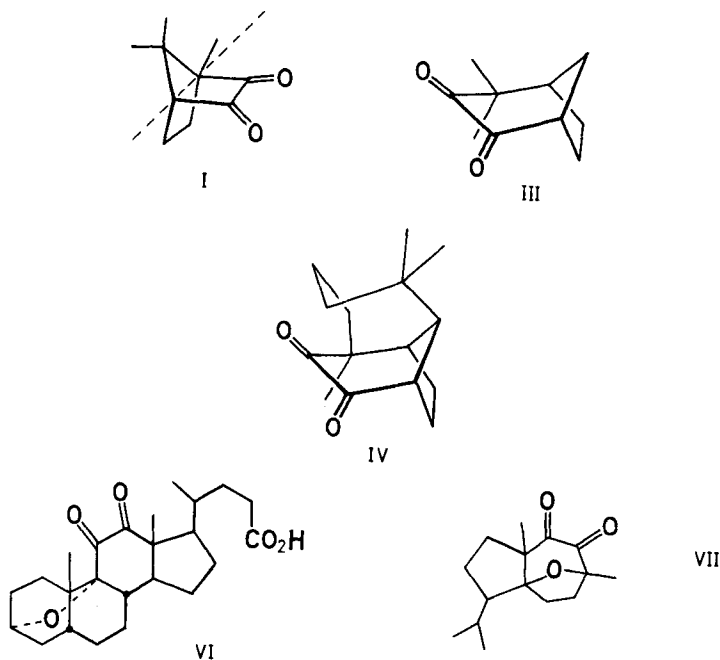
Summary. Our deductions of the chirality of α -diketones from the skewed glyoxal model [2] have recently been questioned [1]. In particular it has been suggested [1] that the longest-wavelength Cotton effect is not determined by the chirality of the chromophore, but rather by contributions from substituents. Arguments against this view are given here and it is concluded that the skewed glyoxal model is still the best starting point for discussion of the optical activity of α -diketones. To settle the question unambiguously, further spectroscopic data are necessary, however.

For a series of α -diketones Burgstahler & Naik [1] question the chirality deduced by us from MO calculations on the twisted glyoxal model [2]. On the basis of these results we predict that for a cisoid righthanded dione chromophore the Cotton effect appearing at longest wavelength (350–500 nm) is positive whereas that at shorter wavelength (260–330 nm) is negative. As explicitly stated in our paper, these predictions are based on the assumption that the inherent chirality of the dione chromophore is the decisive factor in determining the sign and magnitude of the long-wavelength

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Cotton effects in α -diketones and that the influence of adjacent substituents is of lesser importance. *Burgstahler & Naik*, on the other hand, suggest that in such systems, substituents (axial bond) chirality contributions exercise an overriding influence on the longest-wavelength *Cotton* effect (350–500 nm) and that it is possibly only the second *Cotton* effect (260–330 nm) which is more directly related to the inherent chirality of the chromophore. Furthermore, *Burgstahler & Naik* are of the opinion that our steric predictions are not in agreement with *Dreiding* models, and that this should support their demand for a revision of conformational assignments.

Burgstahler & Naik start from molecule VII (α -oxodaucone) the absolute configuration of which has been determined by *Levisalles & Rudler* [3]. If the stereochemistry of VII is as given by these latter authors, then there is in fact strong indication of a righthanded chromophore, in contrast to our prediction. Because of complications in the CD. spectrum [3] [4], by its deviation from that of a typical dione spectrum, this molecule is, however, an unfortunate example, both for and against the twisted glyoxal model²⁾. We think that the spectrum as given [3] [4] cannot be used as a



²⁾ The CD. spectrum of VII as given in Ref. [3] and [4] reads λ ($\Delta\epsilon$): 480 nm (0.), 464 (+0.04), 458 (0.), 406 (-1.60), 358 (0.), 300 (+6.40), 281 (+3.15). The values of λ_{\max} from UV. spectra are [3] 447 nm ($\epsilon = 21$) and 350 nm ($\epsilon = 72$) in cyclohexane. In retrospect we realize that the application of the twisted glyoxal model to this data was premature, for the following reasons: The absorption maxima of the UV. spectrum lie at λ -values where the CD. curve is essentially zero. This lack of consistency may indicate different conformations, strong vibronic interactions, the presence of hydrated forms, or simply an impure product. The very weak positive *Cotton* effect at 464 nm was erroneously disregarded in our discussion and the positive *Cotton* effect at 281 nm, following the positive one at 300 nm, is not consistent with the picture of a typical dione spectrum [2]. In any case, the deduction of empirical rules from VII would require a careful reinvestigation of the low-temperature CD.- and UV.-spectra.

starting point to question our conformational deductions in more typical cases, such as in III and IV and in the steroid VI.

The stereochemical evidence derived from *Dreiding* models alone does not seem convincing to us. In most of the examples cited we have heavy strain of the *Bayer* and *Pitzer* type, and it is well known that under such circumstances *Dreiding* models are no longer a reliable tool for conformational assignments. In molecule IV the answer to the question whether *Dreiding* models favour one chirality of the dione system rather than the other depends on the addition of a number of stabilizing and destabilizing interactions which may hardly be assessed quantitatively. In III the situation is somewhat simpler, and a lefthanded chirality indeed leads to a slightly reduced methyl-methylene interaction. But at the same time the six-membered ring takes on a chair conformation. This is not in accord with the general tendency of six-membered rings containing one or two sp^2 carbon atoms to deviate from normal chair conformations [5]. The steroidal 11,12-diones may be viewed similarly. In 11-oxosteroids low-temperature CD. measurements have revealed an unexpectedly high conformational mobility and a conformation at variance with the results obtained by *Dreiding* models [6]. With the introduction of a second sp^2 carbon in position 12 the mobility of ring C might conceivably be further modified. In 11-ketones the occurrence of ring C both in the chair and in the boat form is an indication that the conformation derived by us for 11,12-diones cannot simply be ruled out.

With respect to the *Cotton* effects of π - π^* transitions in dienes and enones, we agree with *Burgstahler & Naik* that in the cisoid cases the spectral data cannot be accounted for satisfactorily if the influence of the chiral environment of the double bonds is neglected [7]. Because of lack of sufficient experimental data it is difficult to decide at present if, as claimed in [1], this view applies equally well to the 245 nm transition in VI which appears to have strong $n \rightarrow \sigma^*$ character. On the other hand, transitions of the $n \rightarrow \pi^*$ type are of a different symmetry and must be viewed accordingly. We cannot concur with the suggestion made by *Burgstahler & Naik* that the longest-wavelength 400 nm *Cotton* effect in diones is determined by substituent effects, whereas the second one at about 300 nm bears more direct relationship to the inherent chirality of the chromophore. Calculations consistently show these two $n \rightarrow \pi^*$ transitions to be inseparably related, – although energetically strongly split apart –, and *always to lead to Cotton effects opposite to each other in sign*. From the symmetry of the wavefunctions [2] and from spectroscopic evidence [8] one recognizes that it is less the 300 nm *Cotton* effect, but rather the one at 400 nm which is directly related to the 340 nm *Cotton* effect of conjugated enones. This latter *Cotton* effect is quite definitely determined by the inherent chirality of the chromophore [9]. In the few additional examples of planar or almost planar diones given in [1] one of course no longer expects an inherent chirality rule to hold. The two $n \rightarrow \pi^*$ *Cotton* effects are in fact either no longer opposite in sign or show even bisignate character, which may be due to flexibility or solvent effects.

Concerning the chiroptical properties of the cyclopentane diones I and II, the diene analogue discussed by *Burgstahler & Naik* certainly is a good example for the influence of substituent chirality on $\pi \rightarrow \pi^*$ transitions. But we do not see in that any direct evidence against our interpretation of the long-wavelength CD. spectrum of the dione, assuming a righthanded twist of the chromophore under the influence

of the bridgehead methyl. Furthermore, if substituents influence the longest-wavelength *Cotton* effect in the way *Burgstahler & Naik* suggest, they would tend to reinforce the observed positive value, making a distinction between the different origins of the optical activity in that case difficult.

In conclusion we feel that the twisted glyoxal model is still the best starting point for discussing the optical activity of asymmetric α -diketones. As previously reported [2] [10], calculations on twisted glyoxal also interpret very satisfactorily the electronic absorption spectra of α -diones for different angles of twist between the two carbonyl groups, in particular the characteristic variation of the wavelength of the first (longest-wavelength) transition, as well as changes in the relative intensity of absorption of the first and second transition. The evidence furnished against the twisted glyoxal model, as a means of interpreting CD. spectra, does not seem to us sufficient to question its basic applicability. But we agree with *Burgstahler & Naik* that the question of substituent effects should be further pursued, and that additional spectroscopic evidence would be most highly welcome³⁾.

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³⁾ The Publication Committee hereby declares that this reply terminates the discussion of this object in the *Helvetica chimica acta*.

69. Stereochemical Assignment of the Two Isomeric Tropine N-Oxides by Proton Magnetic Resonance at 220 MHz

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Summary. Proton magnetic resonance spectra of tropine and the two isomeric tropine N-oxides have been analysed at 220 MHz. Chemical shifts in the N-oxides are expressed relative to tropine ($\Delta\nu_{\text{NO}}^{\text{N}}$) and permit unequivocal structural assignments of the predominant isomer (**1**, equatorial N-oxide) and the minor isomer (**2**).