Wie uns Herr Prof. *E. Giovannini*, Universität Fribourg, am 9.10.1971 freundlicherweise mitteilte, wurde die Photolyse von 3-Methyl- und 3-Äthyl-anthranil in 66-proz. Schwefelsäure bzw. konz. Salzsäure zu 2-Amino-5-hydroxy- bzw. 5-chloraceto- bzw. -propiophenon schon 1963 von seiner Arbeitsgruppe ausgeführt [21] (vgl. auch [22]).

Wir danken dem *Schweizerischen Nationalfonds* für die Unterstützung dieser Arbeit.

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313. Comment on the Chirality and Cotton Effects of Cyclic α-Diketones: Revision of Recent Conformational Assignments[1]

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(4. XI. 71)

Summary. A recent proposal [1] correlating the *Cotton* effects and dione chirality of various cyclic α-diketones according to a skewed glyoxal model is held to require revision in the light of overriding evidence from molecular models and the effects expected from substituent chirality contributions.

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[1] Published by special decision of the Editorial Committee.

Recently, as the result of calculations pertaining to the nodal properties and chirality of the ground and excited state orbitals of a skewed glyoxal model, *Hug & Wagnière* [1] have suggested that the helicity or chirality of a cisoid 1,2-dione is right-handed when the sign of the 400-nm region (longest wavelength) $n \rightarrow \pi^*$ transition *Cotton* effect is positive and left-handed when it is negative. On this basis they postulated that both (+)-camphorquinone ('5,6-camphorquinone') (I) and isofenchoquinone (II) have a small but detectable right-handed dione chirality. In the same manner they concluded that the nonplanar dione moiety in compounds III–VI is twisted in the form of a right-handed helix, while in compound VII it is left-handed.

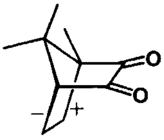
Although well supported by the theoretical considerations they presented, the dione chiralities proposed by these authors for compounds III-VII appear to us to be just the opposite of those favored by molecular models as well as by the effects expected from substituent (axial bond) chirality contributions. In particular, for the rigid dione VII (α-oxodaucone), the absolute configuration of which has been determined by *Levisalles & Rudler* [2], Dreiding *models unequivocally indicate a right-handed dione chirality rather than the left-handed one supposedly implied by the negative 400-nm region* Cotton *effect.* Since the CD. spectral pattern of VII, even though evidently complicated by the presence of the ether function (and perhaps by other factors as well), is basically opposite to that exhibited by compounds III–VI, *it follows that the dione chiralities of the latter are more likely to be left-handed than right-handed.*

Thus, with a right-handed dione chirality in III and IV, as suggested by *Hug & Wagnière*, an unfavorable, nearly eclipsed butane-type methyl-methylene interaction is introduced. But with a left-handed dione chirality, as proposed here, this repulsion is avoided, although in the case of IV the energy difference between the two dione chiralities is admittedly complicated by destabilizing interactions arising from the substituted tetramethylene bridge. However, the identity of the sign patterns of the *Cotton* effects of III and IV strongly supports the view that the two compounds have the same predominant (left-handed) dione chirality.

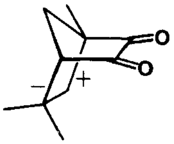
Similarly, although the steroidal 11,12-dione V appears to be considerably enolized in solution [3], its *Cotton* effect sign pattern, like that of the more representative non-enolizable dione VI, points to the same dione chirality as is present in III and IV. Hence a left-handed chirality is also favored for V and VI, with ring C in a chair conformation. In addition, *Dreiding* models suggest that there is significantly less bond-angle distortion, especially in VI, when ring C has the normal chair conformation (left-handed dione chirality) than when it is in the twist-boat form (right-handed chirality).

In regard to substituent chirality contributions in these cyclohexanediones, evidence has been presented recently [4] showing that the sign of the lowest energy $\pi \rightarrow \pi^*$ transition *Cotton* effect of structurally related heteroannular cisoid conjugated dienes and enones correlates well with chirality contributions of allylic axial bonds but not with the inherent chirality of the chromophore. On this basis, the positive low-wavelength *Cotton* effect of VI observed at ~245 nm (and by implication that at ~390 nm) would appear to correspond to the right-handed (positive) chirality contributions of the axial 9α and 13β bonds attached to a left-handed dione system. Although only portions of the required CD. data are available, the same type of inter-

Conformational formulas with revised dione chiralities[2])



I



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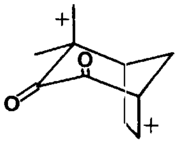
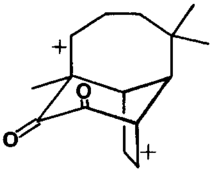


III (L-Helix)



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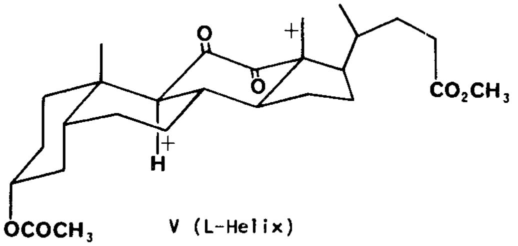

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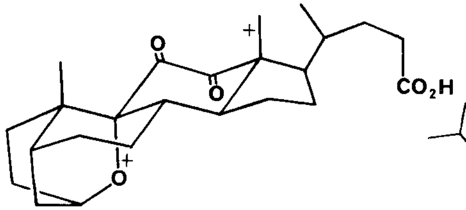

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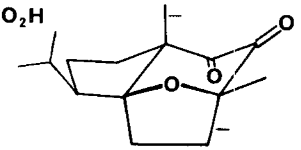
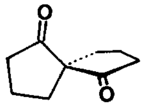


VII (R-Helix)



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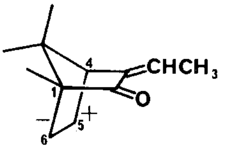
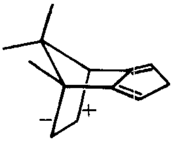


IX



X

pretation presumably also applies to the other diones in this series. By the same token, these revised dione chiralities suggest, at least in the case of compounds III-VII, that it is the intermediate 300-nm region *Cotton* effect and not that in the 400-nm region which bears a more direct relationship to the inherent chirality of the chromophore, just as appears to be the case with the 340-nm region *Cotton* effect of conjugated enones [5].

In contrast to compounds I–VII, the longest wavelength *Cotton* effect of the spiro dione VIII lies at 315 nm, indicating that it probably differs significantly from that in the 400-nm region of I–VII. A similar example in the steroid field but with a negative long-wavelength *Cotton* effect (near 290 nm) and opposite chirality is cited by *Crabbé* [3]. Such β-diketones are analogous to chiral β,γ-unsaturated ketones and

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[2]) The signs + and – designate, respectively, positive and negative axial bond chirality contributions to adjacent π-bonds [4].

1,4-dienes, in which the longest wavelength *Cotton* effect generally does correlate well with the chirality of the interacting π-bonds [6].

With respect to the chiroptical properties of the cyclopentanediones I and II, especially in the low-wavelength region, the closely related enone IX and diene X offer instructive parallels. Enone IX, derived [7] from (+)-camphor, exhibits a strong positive *Cotton* effect ($\Delta\varepsilon \sim +10$) at 235 nm (in hexane) that appears to us to owe its origin primarily to the positive chirality contribution of the rigid allylic 'axial' 4:5 bond to the ethylidene double bond. Similarly, the negative shorter wavelength *Cotton* effect (near 200 nm) then corresponds to the negative chirality contribution of the 1:6 bond to the carbonyl group.

Diene X, prepared by *Wittig* synthesis [8] from (–)-camphorquinone, displays a negative *Cotton* effect at 245 nm ($\Delta\varepsilon = -0.55$) and a positive one at 215 nm ($\Delta\varepsilon = +0.80$), suggesting that in this case the overriding longer wavelength chirality contribution is from the methylated bridgehead side of the molecule. On this basis, the lowest energy $\pi \rightarrow \pi^*$ transition *Cotton* effect exhibited by dione I near 220 nm (and presumably also by II) would likewise appear to reflect a predominance of the 'axial' bond chirality contribution from the bridgehead side bearing the methyl group.

In connection with the longer wavelength *Cotton* effects of I and II, the chiroptical properties of three additional non-enolizable cyclopentane-1,2-diones are of interest for comparison. 3,3-Dimethyl-A-nor-5α-cholestane-1,2-dione and the corresponding 5-ene are seen from *Dreiding* models to have small but definitely left-handed dione chiralities. Yet both exhibit a substantial positive long-wavelength *Cotton* effect ($\Delta\varepsilon \sim +2.1$) in the 450–500-nm region [3], possibly arising from positive chirality contributions of the 10β and 5α (or 5-ene) bonds to the C-1 and C-2 carbonyl groups, respectively. Moreover, the former is reported to have a weak positive *Cotton* effect ($\Delta\varepsilon \sim +0.3$) near 300 nm, while the latter has a somewhat stronger negative one ($\Delta\varepsilon \sim -0.9$) in this region. On the other hand, an analogous five-membered ring α-diketone in the clovane series [3], which appears to have a practically planar dione system, exhibits only a weak double *Cotton* effect in the 500-nm region ($\Delta\varepsilon \sim -0.15$ above 500 nm; $\Delta\varepsilon \sim +0.15$ below 500 nm) but a stronger positive one ($\Delta\varepsilon \sim +1.4$) near 300 nm. Thus, no completely consistent pattern can be discerned, and, in the absence of additional evidence, we conclude that the dione chiralities of I and II, however small, cannot be assigned with certainty simply on the basis of their *Cotton* effects. Obviously, further studies in this area and also on such cyclohexanediones as VI and VII are clearly desirable, especially through *X*-ray and NMR. methods of stereostructure determination.

CD. data for IX and X were measured in hexane in a 1.0-cm cell with a *Cary* Model 60 recording spectropolarimeter equipped with a Model 6001 CD accessory unit and will be reported in detail in connection with other work.

We are grateful to Professor *G. Wagnière*, Mr. *J. K. Gawroński*, and Drs. *J. Hudec* and *W. Hug* for helpful comments and discussions.

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314. Strukturaufklärung zweier Pigmentfarbstoffe der Perylen-Reihe[1])

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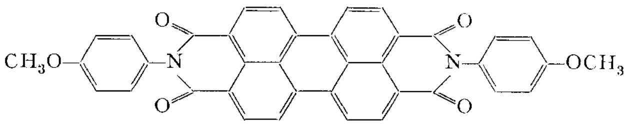
Consiglio Nazionale delle Ricerche
Laboratorio dei composti del carbonio contenenti etero-atomi e loro applicazioni, Ozzano Emilia (Bologna)

(21. X. 71)

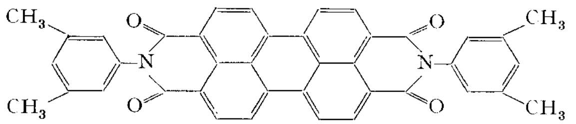
Summary. The structures of *C.I. Pigment Red 149* (*PV Fast Red B*)® and *C.I. Pigment Red 178* (*Paliogen Red GG*)® as II and III respectively, are deduced from elemental analysis, spectroscopic data, and synthesis.

1. C.I. Pigment Red 149 (PV Echtrot B)® ist laut Colour Index [2] ein Perylenfarbstoff. *Lenoir* [3] ordnet ihn in die Gruppe des Perylenrots (I) ein[2]), während er nach *Arient* [6], der sich auf das *Hoechst-Zirkular* Nr. 2395 (1956) bezieht, mit dem bekannten Perylenscharlach (II) identisch ist. Wir haben nun Pigment Red 149 spektroskopisch untersucht und können die Angaben von *Arient* bestätigen.



$C_{38}H_{22}N_2O_6$ (602,6; I)

Perylenrot (*C.I. Vat Red 29*)
C.I. 71140



$C_{40}H_{26}N_2O_4$ (598,6; II)

Perylenscharlach

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[1]) 3. Mitteilung «Über Strukturaufklärung von Pigmentfarbstoffen mit kombinierter Spektroskopie»; 2. Mitteilung s. [1].

[2]) Für die Perylenfarbstoffe haben wir die Benennungen von *Gärtner* [4] und nicht diejenigen von *Schweizer* [5] verwendet.