Structure of Diethyl Glaucophanic Enol in the Crystal, and in Solvents of Differing Polarities

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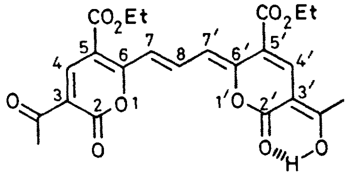
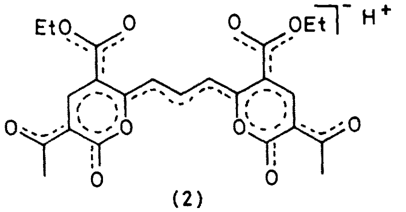
Summary Black diethyl glaucophanic enol crystals have a 'staircase' arrangement of molecules connected by self charge-transfer interactions and display semi-conductance: in dry less-polar solvents ^{1}H n.m.r. and u.v. data support the unsymmetrical enol structure (**1**) but in polar solvents the structure is symmetrical (**2**): comment is made on other glaucyrones, one of which exists in the 7′-*H*-form in $CDCl_3$.

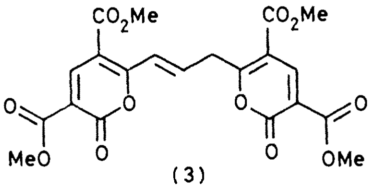
DIETHYL GLAUCOPHANIC ENOL (3,3′-diacetyl-5,5′-diethoxycarbonylglaucyrone) (**1**)[1] forms black crystals from benzene. We have determined their structure by *X*-ray analysis in the hope that it might provide information on the unusual appearance of the crystals. *Crystal data*: monoclinic $P2_1/c$, $a = 9{\cdot}279(3)$, $b = 20{\cdot}823(6)$, $c = 13{\cdot}907(4)$ Å, $\beta = 125{\cdot}65(2)^\circ$, $R = 5{\cdot}1\%$, 2157 independant observed reflections.† Figure 1 shows two projections of adjacent pairs of molecules and Figure 2 shows the packing within the crystal. Approaches of less than the sum of van der Waals radii occur between the pyrone elements of adjacent molecules (*cf.* Figure 1) which indicate charge-transfer interaction.[2] Thus the C-2 (carbonyl) to C-3′ (chelate ring carbon) approach distance is 3·27 Å and the C-4 to C-5′ distance is 3·39 Å. One pyrone may be viewed as an acceptor *via* the α-unsaturated carbonyl ring, the other as a donor *via* C-3′ of the chelate ring and the conjugated C-5′ terminus. The charge transfer interaction is reversed at the other pyrone ring of an individual molecule leading to a step-wise arrangement of conjugated molecules running through the crystal, connected by self charge-transfer interactions:



(1)



(2)



(3)

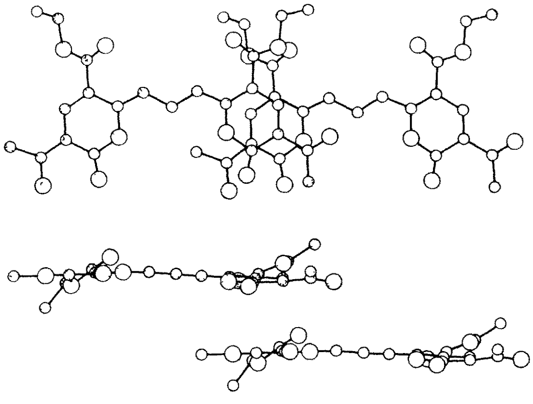
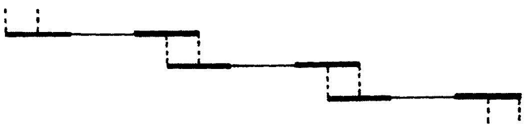


FIGURE 1. Two views of pairs of diethyl glaucophanic enol molecules which have short intermolecular contacts.



Separation between pairs of 'staircases' is increased because the ester appendages are twisted out of plane. Single crystal electrical conductance measurements have not yet been made but the compaction measurement at room temperature is $5{\cdot}2 \times 10^{-8}\,\Omega^{-1}\,\mathrm{cm}^{-1}$,§ rather high for a pure organic solid (usually $< 10^{-12}\,\Omega^{-1}\,\mathrm{cm}^{-1}$). The self charge-transfer structure is consistent with the black colour of the crystals.

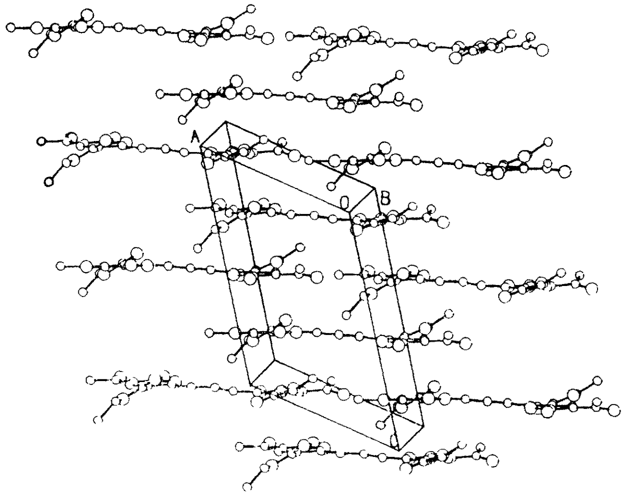


FIGURE 2. Diethyl glaucophanic enol, arrangement of molecules in the crystal

In dry $CDCl_3$ solution (red colour) diethyl glaucophanic enol exists in the enolic form (**1**) (C-7, -8, and -7′ protons form an AMX pattern, τ 2·40, 1·84, and 3·01, J 15 and 12 Hz, chelated hydroxy − 3·85)‡ but in wet $(CD_3)_2SO$ (blue solution) n.m.r. data show a symmetrical structure (**2**), data for the two pyrone rings and the 7- and 7′-hydrogens being undifferentiated (8-H, t, 1·84, J 13·7 Hz). These data are complemented in the u.v. spectrum. In less polar solvents, chloroform or benzene, the u.v. data [*e.g.*, λ_{max} $(CHCl_3)$ 503 ($\epsilon \times 10^{-3}$, 43·4), 354 (11·4), 332 (12·7), and 296 (6·6) nm] differ markedly from those in polar solvents such as ethanol, dimethylsulphoxide, dimethylformamide, or propylene carbonate [*e.g.*, λ_{max} (Me_2SO) 678 ($\epsilon \times 10^{-3}$, 124·8), 641

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Spectra (^1H and ^{13}C n.m r.) in ordinary (damp) $CDCl_3$ lie in the slow exchange region though the central 8-H or C-8 resonance remains sharp.

(inflection) (35·9), 428 (11·7), 396 (17·5), 376 (inflection) (12·2), 334(7·0), 285 (8·8), and 268 (17·2) nm]. The u.v. spectrum of diethyl glaucophanic enol in ethanol is closely similar to that of its sodium salt showing the enol to be almost completely ionised in polar solvents. Dry acetonitrile and acetone show intermediate behaviour as solvents, and spectra are very sensitive to the presence of water.

3-Acetyl-3′,5,5′-trimethoxycarbonylglaucyrone[3] shows ^{1}H n.m.r. and u.v. spectral behaviour similar to (**1**)/(**2**), though the deprotonated form is necessarily not symmetrical. 3,3′,5,5′-Tetramethoxycarbonylglaucyrone[3] on the basis of ^{1}H n.m.r. data, exists in dry $CDCl_3$ in the 7′-*H*-form (**3**) [7-H, 2·46, d, *J* 15 Hz; 8-H, *ca.* 2·94 m; 7′-H (2H) 5·84, d, *J* 6·4 Hz]. In wet $(CD_3)_2SO$, however, it has the deprotonated symmetrical form.

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[3] S. R. Baker and L. Crombie, *J. Chem. Soc., Chem. Commun.*, 1980, 213.

§ We thank Dr. G. J. Ashwell for this measurement.