

Charge-transfer and Non-charge-transfer Crystal Forms of (*E*)-5,5'-Dimesitylbifuranylidenediones: an X-Ray Structural Investigation

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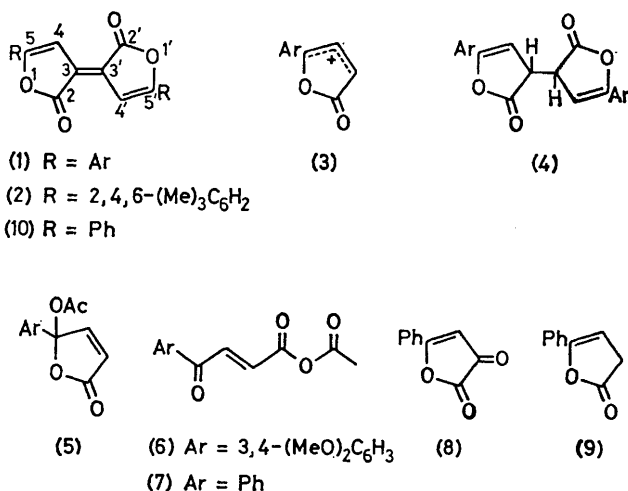
Summary Synthesis of compounds of type (1) is briefly considered: X-ray study shows the dimesityl representative (2) to exist in a self charge-transfer form as very dark blue-black needles having a metallic lustre, and in a scarlet non-CT form; the preparation and interconversion of the forms is mentioned.

5,5'-DIARYLBIFURANYLIDENEDIONES of type (1) ('Pechmann dyes')¹ are readily formed by treatment of aroylacrylic acids with acetic anhydride in the presence of Cu^I catalyst.² Following our discovery of the self charge-transfer structure of diethyl glaucophanic enol,³ we were attracted by the metallic sheen displayed by the beautiful and highly coloured crystals of certain compounds of type (1) and report below on the X-ray structures of two crystalline forms of the 5,5'-dimesityl compound (2). No explanation of the formation

of (1) was given by Fang and Bergmann² and we suggest that such compounds are formed (in yields up to 80%) by one-electron transfer to the cation (3), radical coupling, and aerial dehydrogenation of (4). The cation (3) may originate by solvolysis of the acetyl-lactol (5) but we have found that when the reaction is carried out in the absence of air, a mixed anhydride (6) can be isolated (yellow needles, m.p. 113–115 °C; ν_{\max} 1805, 1715, and 1655 cm⁻¹; n.m.r., olefinic protons, J 16 Hz). The latter is an intermediate, as treatment with Cu^I in acetic anhydride and air gives [1, R = 3,4-(MeO)₂C₆H₃].[†] We also find that the bifuranylidenedione system (10) can be made (50%) from benzoylpyruvic acid by refluxing with acetic anhydride and triethyl phosphite; the lactone (8) is presumably formed and deoxygenated to a carbene intermediate. Heating the lactone (9) with active manganese dioxide in air also gave (10) in about 40% yield via the radical coupling pathway.

The dimesityl compound (2)⁴ crystallised from xylene (or toluene or benzene) in superb, long, very dark, blue-black needles with a metallic lustre. On heating, an abrupt change to a brilliant scarlet form occurred (139–142 °C)[‡] and this melted at 284–287 °C. The scarlet form is the stable form and could be produced by crystallising the blue-black crystals from polar solvents such as dimethylformamide, dimethyl sulphoxide, or acetic acid; the identity of the scarlet forms produced in the two ways was demonstrated by X-ray powder diffraction. In solution the blue-black and scarlet forms of (2) had identical u.v. spectra, but measured as KBr discs i.r. spectra were distinctive. It seems clear that molecular solvation is an important factor in deciding which type of lattice is laid down by crystallisation.

The blue-black monoclinic crystals (space group $P2_1/c$) had $a = 3.966(1)$, $b = 16.436(3)$, $c = 15.613(3)$ Å, $\beta = 96.81(2)^\circ$, $Z = 2$, and were subjected to single crystal X-ray analysis (1172 independent observed reflections) and refined



[†] A mixed-anhydride (7) showing the same behaviour has also been isolated when Ar = Ph by Miss B. A. H. Darwish in our laboratory.

[‡] The transition temperature may vary with crystal size, and the figure given relates to powdered material. Large crystals retain their overall shape but the new red 'crystal' is crazed and appears disordered on single-crystal X-ray examination.

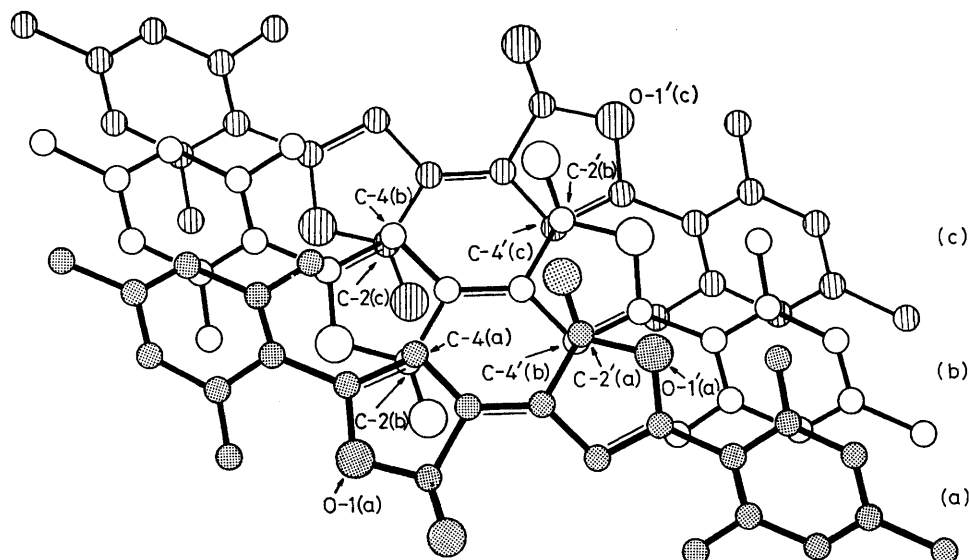


FIGURE 1. Arrangement of molecules of the dark blue-black form of the dimesityl compound (2) in the crystal.

to $R = 7.9\%$.[§] Figure 1 shows the arrangement of adjacent molecules in the crystal whilst Figure 2 shows the angle of twist (39°) of the mesityl rings relative to the furanylidene

section. Adjacent molecules take up an arrangement reminiscent of overlapping roof-tiles and may be represented as in (A). In the system of three molecules shown (Figure 1)

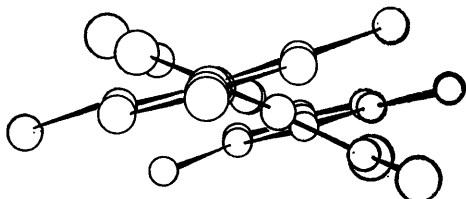
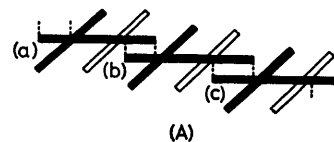


FIGURE 2. Dark blue-black form of the dimesityl compound (2).



the molecule in the middle of the 'sandwich' has C-4(b) and carbonyl C-2'(b) lying above C-2(c) and C-4'(c) respectively whilst carbonyl C-2(b) and C-4'(b) lie under C-4(a)

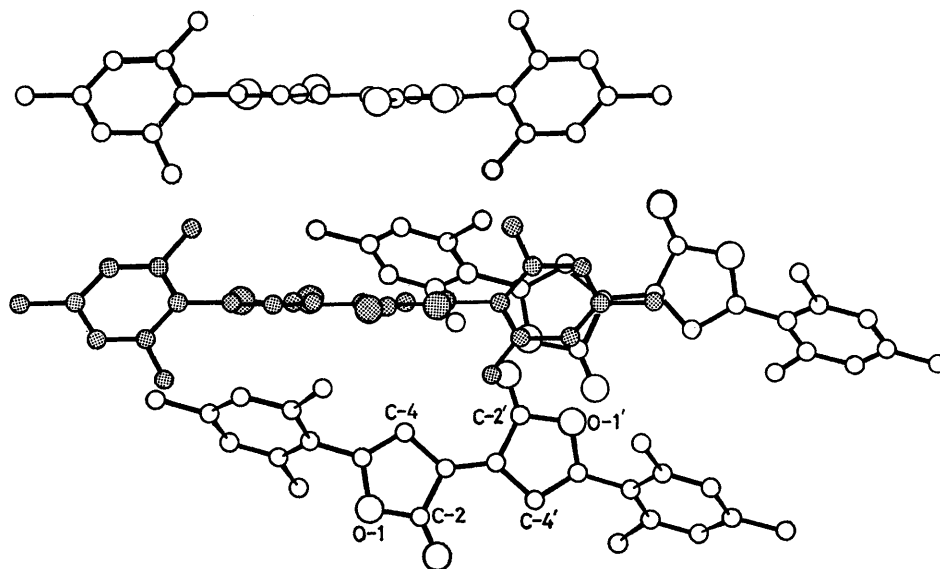


FIGURE 3. Arrangement of molecules of the scarlet form of the dimesityl compound (2) in the crystal.

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

and carbonyl C-2'(a) respectively. These four identical intermolecular contacts are 3.31 Å, constituting close approaches characteristic of a charge-transfer interaction (usually taken as < 3.4 Å).⁵ The mean separation of planes in this crystal are arranged in continuous charge-transfer overlaps throughout the molecular stack. C-2 and C-2' of the carbonyls provide positive centres and C-4 and C-4' positions of electron excess with the O-1 and O-1' lone pairs, and possibly the twisted mesityls, supplying electron density. Superposition of potentially interactive sites occurs, with each individual molecule having donor and acceptor properties towards adjacent molecules.¶

X-Ray analysis of the stable monoclinic red crystals ($P2_1/n$), $a = 7.923(2)$, $b = 7.735(2)$, $c = 17.854(3)$, $\beta = 109.32(2)^\circ$, $Z = 2$, was carried out using 1761 observed reflections and refined to $R = 4.5\%$.§ The structure has a totally different crystal arrangement as shown in Figure 3. No abnormally short van der Waals contacts are present and the angle of twist of the mesityl rings is now substantially increased (56°) relative to the blue-black form (Figure 4). The smaller (39°) angle of the blue-black form is dictated by

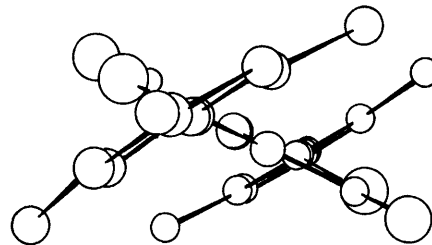


FIGURE 4. Scarlet form of the dimesityl compound (2).

steric restraints of the lattice but it may allow some contribution, by electron release to the furan units, to the molecular interactions that stabilise the arrangement. In solution the out-of-plane character of the mesityl rings of (2) is clearly revealed when its u.v. spectrum [$\lambda_{\max}(\text{CHCl}_3)$ 468 (ϵ 27,900) and 271 nm (9000)] is compared with that of the phenyl analogue (10) [$\lambda_{\max}(\text{CHCl}_3)$ 535 (ϵ 40,500), 505 (42,700), 288 infl. (21,900), and 281 nm (23,300)].

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¶ The electrical conductivity measured as a compaction is little different from that of a normal organic compound and photoconduction was not displayed. However, during the latter examination it was found that the blue-black form was converted photo-physically into the red in the solid state. We thank Dr. M. Willis of this Department for the information.

¹ E. Klingsberg, *Chem. Rev.*, 1954, **54**, 59.

² C. S. Fang and W. Bergmann, *J. Org. Chem.*, 1951, **16**, 1231.

³ S. R. Baker, M. J. Begley, and L. Crombie, *J. Chem. Soc., Chem. Commun.*, 1980, 390; *J. Chem. Soc., Perkin Trans. 1*, 1981, 182

⁴ T. Kozniowski and L. Marchlewski, *Bull. Acad. Sci. Crakow*, 1906, 81 (*Chem. Zbl.*, 1906, II, 1189).

⁵ S. C. Wallwork, *J. Chem. Soc.*, 1961, 494.