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Tribochromic compounds, exemplified by 3-dicyclopropylmethylene-5-dicyanomethylene-4-diphenylmethylenetetrahydrofuran-2-one

Abdullah M. A. Asiri, Harry G. Heller,* Michael B. Hursthouse and Alexander Karalulov

Chemistry Department, Cardiff University, PO Box 912, Cardiff, UK CF1 3TP. E-mail: heller@cardiff.ac.uk

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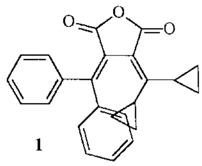
The title compound 2 is obtained as bright yellow metastable crystals, which on mechanical grinding change to the dark red stable form; unlike piezochromic compounds, the reverse colour change does not occur; X-ray crystallographic analyses shows that the yellow form has a folded structure while the red form has a twisted structure.

We introduce the term 'tribochromism' (Greek tribos rubbing, khroma colour) to describe the new phenomenon of metastable crystals that undergo a major and irreversible colour change on mechanical grinding. The coloured form is stable and does not undergo the reverse change when kept in the dark, on heating or when dissolved in an organic solvent. In contrast, piezochromism[1] defines stable crystals, which give highly coloured metastable forms on fracture, which undergo the reverse colour change under the conditions described above.

As part of our studies[2] on photochromic dicyanomethylene derivatives, the severely overcrowded 3-dicyclopropylmethylene-5-dicyanomethylene-4-diphenylmethylenetetrahydrofuran-2-one **2** was prepared by reaction of dicyclopropylmethylene(diphenylmethylene)succinic anhydride **1** with malononitrile in THF in the presence of diethylamine (2 equiv.) at room temperature. The resulting colourless salt was filtered off and treated with acetyl chloride in dichloromethane. Solvent and acetyl chloride were removed and the residue purified by chromatography on silica gel using ethyl acetate and light petroleum (bp 60–80 °C) as eluent. The deep red solution, on concentration, gave a first crop of bright yellow crystals **2y** (*ca.* 0.3 g) and a second crop of dark red crystals **2r** (*ca.* 0.1 g). Red crystals and yellow crystals gave red solutions that showed identical NMR and UV/visible spectra. Repeat experiments with recrystallisation from different solvents gave only red crystals. The deep red solutions gave only red crystals when seeded with yellow crystals. X-Ray crystallographic analysis (which presented difficulties with refinement) on the best of the crude yellow crystals **2y** showed that the diphenylmethylene group is folded (one phenyl lies above a cyclopropyl group and the other above a cyano group). [X-Ray crystallographic analyses on compound **3c(y)**, which was obtained only as tribochromic yellow crystals, showed a folded structure also.] X-Ray crystallographic analysis† of dark red crystals **2r** showed that the diphenylmethylene group is twisted (one phenyl lies above a cyclopropyl group and the other below a cyano group) (Fig. 1).



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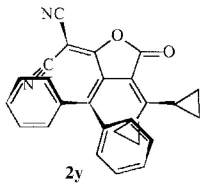
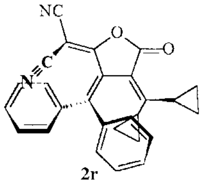


2y



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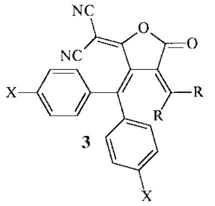

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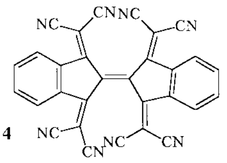

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Gompper[3] has reported that di[1,1-bis(dicyanomethylene)-indan-2-ylidene] **4** exists in yellow and in red crystal modifications and that X-ray crystallographic analysis showed that in yellow crystals, molecules have a folded structure whereas in red crystals, molecules have a twisted structure.

The tribochromic properties were discovered accidentally. Since yellow crystals **2y** gave deep red solutions, it was not possible to observe whether compound **2y** was photochromic in solution. To produce a greater surface area to test for

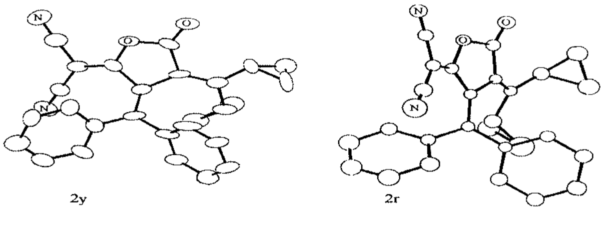

Fig. 1 X-Ray structures of yellow crystals **2y** and red crystals **2r**.

Table 1 Melting points, yields, and λ_{max} values of long wavelength absorption bands for solutions measured in toluene for overcrowded molecules **2** and **3a**–**i**, indicating whether they are obtained as yellow tribochromic crystals (**y**) or dark red stable crystals (**r**)

Compound	$R_2C=$	X	Mp/°C[a]	Yield(%)	λ_{max}/nm
2(y)[c]	dicyclopropylmethylene	H	183–4	21[b]	503
2(r)[c]	dicyclopropylmethylene	H	188–9	7	503
3a(y)	dicyclopropylmethylene	F	203–5	59	510
3b(y)	dicyclopropylmethylene	Cl	197–8	42	514
3c(y)[c]	isopropylidene	H	182–3	55	479
3d(r)	isopropylidene	F	185–8	45	484
3e(r)	isopropylidene	Cl	193–4	66	484
3f(y)	adamantylidene	H	213–5	56	486
3g(y)	adamantylidene	F	235–7	36	495
3h(y)	adamantylidene	Cl	245–7	48	503
3i(r)[c]	cyclopentylidene	H	162–4	41	489

[a] Gave deep red melts. [b] An unrepeatable reaction. [c] X-Ray analysis showed that yellow forms **2(y)** and **3c(y)** have folded structures and red forms **2(r)** and **3i(r)** have twisted structures.

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photochromism in the solid state by irradiation with ultraviolet light, yellow crystals were ground with a spatula. On grinding, they turned dark red.

A range of related compounds **3a–i** has been prepared in which the dicyclopropylmethylene group was replaced by 2-propylidene, adamantylidene and cyclopentylidene groups and in which 4-hydrogens on the phenyl groups were replaced by chloro and fluoro groups. Compounds were obtained either as yellow or dark red crystals (see Table 1) but never in both forms with the exception of **2y** and **2r**. All compounds obtained as yellow crystals were tribochromic.

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Notes and references

† *Crystal data* for **2y**: $C_{27}H_{20}N_2O_2$, M = 404.4, monoclinic, space group $C2/c$, a = 10.07(3), b = 23.91(5), c = 9.50(5) Å, β = 110.4(2)°, V = 2144(13) Å^3, T = 293(2) K, Z = 4, D_c = 1.253 g cm^{-3}, R_1 = 0.0897, wR_2 = 0.2076 for all 2629 data and 257 parameters. For **2r**: $C_{27}H_{20}N_2O_2$, M = 404.4, monoclinic, space group $P2_1/c$, a = 20.349(2), b = 10.095(2), c = 21.338(2) Å, β = 99.06(2)°, V = 4328.6(13) Å^3, T = 293(2) K, Z = 8, D_c = 1.241 g cm^{-3}, R_1 = 0.0640, wR_2 = 0.1743 for all 5500 data and 282 parameters. Data were recorded using a FAST TV area detector diffractometer and Mo-Kα radiation. CCDC 182/1589. See http://www.rsc.org/suppdata/cc/b0/b001567i/ for crystallographic files in .cif format.

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