Photochromism in Organomercury(II) Dithizonates

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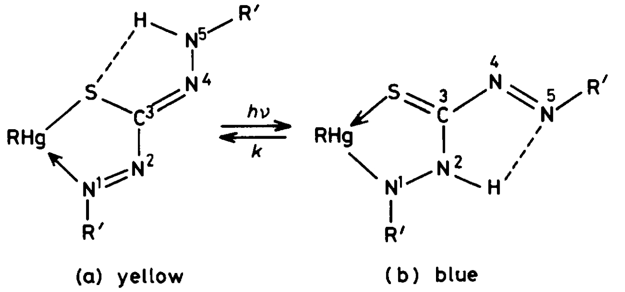
1 : 1 Complexes of organomercury(II) cations HgR^+ (R = Me, Ph, 2,6-dimethylphenyl, or 2,4,6-trimethylphenyl) and dithizone (and its *p*- and *o*-tolyl homologues) undergo reversible photoisomerization (yellow $\rightleftharpoons$ blue) at conveniently measurable rates when dissolved in organic solvents. Structures for the isomers are deduced from visible, i.r., and ^{1}H n.m.r. spectroscopy, measurements on the labile blue photoisomer being made on irradiated solutions.

Dithizone [1,5-diphenylthiocarbazone, PhN=N–C(SH)=N–NHPh $\rightleftharpoons$ PhN=N–CS–NH–NHPh, abbreviated here as H_2dptc] forms strongly coloured complexes with many heavy metals and has extensive applications in analytical chemistry.[1,2] Irradiation by visible light of solutions of mercury(II) bis(dithizonate) $[Hg(Hdptc)_2]$ (1) [IUPAC nomenclature: bis(1,5-diphenylthiocarbazonato-*NS*)mercury(II)] in organic solvents induces a reversible colour change from yellow to blue, the normal form having a strong absorption band at 485 nm in chloroform which is replaced in the activated form by a band at 604 nm. Although the photochromic behaviour of mercury(II) bis(dithizonate) was first reported by one of us in 1949 [3] and independently by Reith and Gerritsma [4] and later by Webb *et al.*,[5] it was not until 1965 that Meriwether *et al.*[6,7] examined the phenomenon in detail. They showed that photochromism was observable in all heavy metal dithizonates but, apart from the mercury(II) complex (where the half-life of the blue form is of the order of a minute), the rates of the thermal return reactions (blue→yellow) were too fast for conventional measurements. From kinetic studies they proposed [7] the equilibrium shown in the Scheme [(1a) $\rightleftharpoons$ (1b)] where the structure of only one of the ligands is shown in detail. Recent studies using continuous and laser pulse photolysis [8] have elucidated details of the kinetics but the actual structures of the two forms were not discussed.

Although the structure of the stable yellow form of mercury(II) bis(dithizonate) has been established by *X*-ray crystallography [9] as (1a) (showing rather distorted tetrahedral co-ordination about Hg) it has proved impossible to isolate crystals of the blue isomer; even when the solvent is cautiously removed from a (blue) chloroform or benzene solution under continuous irradiation by an intense source of visible light, only the stable yellow form separates.[10] Although this is also the case with the 1 : 1 organomercury(II) complexes of dithizone which form the subject of the present paper, their solubilities in organic solvents are fully one hundred times that of $[Hg(Hdptc)_2]$ (1) [11] where the concentration of even a saturated solution in CCl_4 restricts reliable spectroscopic measurements. Moreover, the rates of the photoisomerism (yellow→blue) are sufficiently rapid and those of the return reactions (blue→yellow) slow enough to produce adequate steady-state concentrations of the labile blue forms to permit useful spectroscopic measurements even by n.m.r. spectroscopy. A preliminary account of this work has already appeared.[12]



	R	R′
(1)	Hdptc	Ph
(2)	Ph	Ph
(3)	$C_6H_3Me_2$-2,6	Ph
(4)	$C_6H_2Me_3$-2,4,6	Ph
(5)	Me	Ph
(6)	Me	*p*-tolyl
(7)	Me	*o*-tolyl

Scheme

Results and Discussion

A number of new 1 : 1 complexes of aryl- and methyl-mercury(II) with dithizone and its *p*- and *o*-tolyl homologues have been prepared and characterized [Scheme, Table 1, compounds (2)—(7); IUPAC nomenclature: (1,5-diarylthiocarbazonato-*NS*)organomercury(II)]. We have carried out *X*-ray crystal structure determinations of both phenyl- and methyl-mercury(II) dithizonates [(2) and (5)] [13] and established the structure of the stable yellow form as (a) (Scheme). In both structures the mercury atom exhibits planar, irregular three-co-ordination, the geometry at the mercury atom being approximately T-shaped. As noted in the case of the $[Hg(Hdptc)_2]$ (1) it has again not proved possible to isolate crystals of the blue isomers from solution and photoisomerization does not appear to proceed at a measurable rate in the absence of a solvent.

The organomercury(II) dithizonates (2)—(7) show very similar spectral properties (Table 2) to $[Hg(Hdptc)_2]$ (1), indicating that the replacement of one of the two dithizone residues by an alkyl or an aryl group does not significantly alter the behaviour of the remaining one. The diffuse reflect-

Table 1. Yields, melting points, and analytical data

			Analyses (%) [a]		
Compound	Yield (%)	M.p. (θ_c/°C)	C	H	N
(1)	69	223—224 [b]	43.5 (43.9)	3.0 (3.1)	15.7 (15.8)
(2)	62	172—173	42.4 (42.8)	3.1 (3.0)	10.5 (10.5)
(3)	69	197—199	46.5 (46.9)	4.0 (4.1)	9.2 (9.5)
(4)	56	184—186	48.2 (48.6)	4.3 (4.6)	9.1 (9.1)
(5)	64	152—155	35.4 (35.7)	2.9 (3.0)	11.8 (11.9)
(6)	52	149—151	38.2 (38.5)	3.5 (3.6)	11.1 (11.2)
(7)	61	158—159	38.3 (38.5)	3.2 (3.6)	11.0 (11.2)

[a] Calculated values are given in parentheses. [b] Lit. 215—216 (ref. 3), 225—226 (ref. 5), 228—229 °C (refs. 6 and 8).

Table 2. Visible absorption, i.r., and ^{1}H n.m.r. spectral data for normal yellow and (in parentheses) activated blue forms

	Absorption maximum/nm		ν(N-H)/cm^{-1}		Chemical shift/p.p.m. [a]		
Complex	Solid [b]	Solution in $CHCl_3$ [c]	Solid [d]	Solution in CCl_4	δ(N*H*) [e]	δ(C*H*$_3$)	δ(HgC*H*$_3$)
(1)	480	485 (604) [7 050]	3 250	3 275 (3 344)	9.21 (10.52)	—	—
(2)	475	470 (609) [3 500]	3 253	3 277 (3 346)	9.19 (10.46)	—	—
(3)	475	471 (608) [4 450]	3 256	3 276 (3 347)	9.20 (10.48)	2.44 (2.45) [f]	—
(4)	470	467 (610) [4 800]	3 252	3 274 (3 340)	9.19 (10.49)	2.33 (2.33) [f] 2.39 (2.40) [f]	—
(5)	480	480 (608) [3 800]	3 255	3 277 (3 344)	9.14 (10.46)	—	1.10 (1.26)
(6)	477	479 (611) [3 950]	3 255	3 276 (3 344)	9.10 (10.45)	2.32 (2.32) [g] 2.40 (2.40) [g]	1.11 (1.25)
(7)	477	480 (608) [3 750]	3 258	3 280 (3 346)	9.15 (10.42)	2.42 (2.42) [h] 2.60 (2.60) [h]	1.09 (1.23)

[a] 90 MHz ^{1}H n.m.r. spectra of $CDCl_3$ solutions at ambient temperature. Shifts are relative to $SiMe_4$. [b] Diffuse reflectance spectra: all broad peaks. [c] Absorption coefficient [ε/m^2 mol^{-1}] given for yellow form only. [d] KBr pressed discs. [e] Disappears on addition of D_2O. [f] Ligand methyl group (R). [g] Methyl of *p*-tolyl. [h] Methyl of *o*-tolyl.

ance spectra of all the solids show a broad peak between 470 and 480 nm, while the normal yellow forms in chloroform solution exhibit absorption maxima from 470 to 485 nm. The i.r. spectra indicate that the normal yellow forms all possess a strongly hydrogen-bonded NH group: this is known from the *X*-ray analyses [13] to be hydrogen-bonded to sulphur. The small shift in ν(N-H) on passing from the solid to solution indicates that this intramolecular N-H $\cdots$ S hydrogen bond is present in both the solid state and in solution. These observations allow the assumption to be made that the *X*-ray analyses determine the configuration of the ligand both in the solid and in solution, namely as in (a) (Scheme). It is interesting to note that the absorption coefficient values for the absorption bands in the organomercury(II) complexes are virtually half of the value found for [Hg(Hdptc)$_2$] (1), where, of course, there are two identical absorbing chromophores. The absorption coefficients for the blue forms were not obtained because of the difficulty of obtaining a steady-state concentration of 100% of this activated form. However, an estimate of *ca.* 1 700 m^2 mol^{-1} for the blue forms of the 1 : 1 organomercury(II) dithizonates is reasonable in view of the values 3 900 and 2 700 m^2 mol^{-1} reported for the blue form of the 1 : 2 mercury(II) bis(dithizonate) in benzene.[7,8]

The i.r. spectral shift of the ν(N-H) band produced on irradiation and consequent photoisomerization is 66—71 cm^{-1} in the organomercury(II) dithizonates and 69 cm^{-1} in [Hg(dptc)$_2$]. Since the shift is to higher wavenumber in every case, this indicates a weaker hydrogen bond in the blue forms and is consistent with the formation of an N-H $\cdots$ N hydrogen bond to the weakly basic azo-nitrogen atom. The N-H $\cdots$ S hydrogen bond is strengthened in structure (a) (Scheme) by a number of possible resonance hybrids which place a negative charge on the sulphur atom as well as by the strong polarization of the mercury–sulphur bond. The difference in wavenumber is the same as that found for the two isomers of *S*-methyldithizone, PhN=N-C(SMe)=N-NHPh, which we have shown to exhibit *syn–anti* isomerism between forms containing N-H $\cdots$ N and N-H $\cdots$ S hydrogen bonds.[14] In the compounds (1)—(7) the N-H $\cdots$ S hydrogen bond is certainly broken on activation and *anti–syn* isomerization about the C=N bond must be followed by electronic rearrangement and an N(5) to N(2) hydrogen transfer which establishes the new but weaker hydrogen bond. It may be assumed that no direct intramolecular hydrogen transfer between nitrogens occurs and it has been suggested [7] that a water molecule, or a second molecule of complex, or both, must serve as a proton bridge, the activated complex for this reaction probably being a complex structure consisting of several water and dithizonate molecules bound together by hydrogen bonds. This hypothesis was supported by the dependence of the return rate on the concentration of water and complex, by the rapid deuterium exchange of the complex (deuteriation slowing the back reaction by a factor of *ca.* three), and the observed pH and solvent sensitivity of the photochromic reaction.[7] The resulting activated structure (b) (Scheme) represents a drastically altered chromophore containing a thiocarbonyl group; many organic compounds with this chromophore in a conjugated system are known to be blue,[15] with visible absorption bands in the same region (580—610 nm) as in the activated forms of the mercury and organomercury dithizonates. It cannot, however, be regarded as a unique explanation because photochromism persists when mercury(II) dithizonate is incorporated in solid media (*e.g.*, glasses or resins) or when the residue $^-$Hg(Hdptc) is present in photochromic polymers or fibres.[16]

The ^{1}H n.m.r. spectra of the stable yellow forms of (5)—(7), all of which contain methylmercury, showed the $HgCH_3$ singlet at $\delta(CDCl_3)$ *ca.* 1.10 (Table 2). Irradiation by an intense beam of visible light using glass-fibre optics enabled the n.m.r. spectra of the blue photo-isomers to be recorded and a downfield shift of the Hg_3CH resonance by *ca.* 0.15 p.p.m. was observed, indicating a change in the character of the ligand donor atoms and pointing again to a thiocarbonyl group in the blue isomer. That these electronic effects are transmitted through the mercury atom was established by changing R in [HgR(Hdptc)] and monitoring the effect on the dithizonate chromophore (Table 2). The coupling constant $^2J(^{199}Hg-^1H)$ in $HgCH_3X$ is known to vary considerably with the nature of X,[17] and although a $^2J(^{199}Hg-^1H)$ of 180.4 Hz was observed in the stable yellow form of [HgMe(Hdptc)] (5), the ^{199}Hg satellite peaks were unfortunately not observed in the spectrum of the activated blue form due to a high noise level. It will be seen from Table 2 that on irradiation no new peaks were observed arising from any of the methyl groups attached to either the arylmercury(II) or dithizonate rings, and it is assumed that any changes were too small to be resolved. This seems reasonable considering the not dissimilar arrangement of the aryl rings in the yellow and proposed blue forms of the ligand residues in complexes (6) and (7) (Scheme), while probably the effect of the photoisomerization is not large enough to affect the shielding of the methyl groups on the arylmercury(II) rings in [Hg(Hdptc)($C_6H_3Me_2$-2,6)] (3) and [Hg(Hdptc)($C_6H_2Me_3$-2,4,6)] (4) (Scheme) to any marked extent. The formation of a different kind of hydrogen bond in the activated form is clearly seen in the disappearance on photoirradiation of the NH resonance at δ *ca.* 9.2 and the appearance of a new resonance at δ *ca.* 10.5 in the activated forms of all the complexes studied.

These results show that the organomercury(II) dithizonates (2)—(7) are photochromic in the same way as $[Hg(Hdptc)_2]$ (1) and, in the absence of crystals of the blue photoisomer, provide evidence in support of Meriwether's[7] proposed scheme for the photochromic reaction of $[Hg(Hdptc)_2]$, (1a) $\rightleftharpoons$ (1b) (Scheme).

Experimental

Preparative.—Arylmercury(II) chlorides were synthesized by reported methods[18] and these or methylmercury(II) acetate (Ventron, Alfa Division) were shaken in stoicheiometric ratios with the appropriate thiocarbazone[10,19] in a 1 mol dm^{-3} aqueous ammonia–benzene extraction system for 10 min. The bright red organic phase was washed with water, aqueous ammonia (1 mol dm^{-3}), and finally with water. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness at room temperature. Recrystallization from benzene–ethanol or benzene–n-hexane gave red-brown microcrystalline products. The analyses, melting points, and yields are collated in Table 1.

Spectroscopic.—The light source used in the visible absorption and i.r. experiments was a 500 W tungsten bulb housed in a standard manual 35-mm slide projector. Infrared radiation was absorbed by 2 cm of water in a glass cell. The visible spectra of the blue forms were recorded on a Varian Superscan 3 by irradiating the sample in chloroform (*ca.* 10^{-5} mol dm^{-3}) in a standard 1-cm quartz optical cell to produce the colour change and then scanning the region of interest at a rapid rate. Periodic scans then allowed the return reaction to be monitored. Suitable i.r. spectra in the N–H stretching region were obtained in a similar fashion on a Perkin-Elmer 180 spectrophotometer using carbon tetrachloride solutions (*ca.* 10^{-2} mol dm^{-3}) in 1-cm silica optical cells. Diffuse reflectance spectra were taken as Nujol mulls on filter paper using a Beckman DK-2A ratio recording spectrophotometer in the reflectance mode. The ^{1}H n.m.r. spectra were obtained at 90 MHz on a Bruker WH-90DS spectrometer operating in the Fourier-transform mode at ambient temperature. Photoirradiation was achieved *in situ* by focusing a pencil-thin beam of light supplied by a Schott Mainz KL 150 B light source (150 W) into the open end of the n.m.r. tube positioned in the magnet, using a glass-fibre optical system. When trying to observe the activated blue form of the complexes special care was taken in cleaning the optical cells and n.m.r. tubes so as to remove traces of impurity which might accelerate the return reaction. Chloroform, carbon tetrachloride, and deuteriochloroform were purified and scrupulously dried. The use of pure and dry solvents ensures a sufficiently long half-life of the activated blue form for spectroscopic measurements to be made.

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