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Photochromic Long-chain Organomercury(II) Dithizonate Complexes in the Azomethine Series

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The synthesis and characterization of a series of 4-(4′-n-alkoxybenzylideneimino)phenylmercury(II) dithizonates, [$C_nH_{2n+1}OC_6H_4CH{=}NC_6H_4Hg(Hdptc)$] ($H_2dptc$ = 1,5-diphenylthiocarbazone = dithizone; *n* = 1, 4, 12, 14 or 18), is described. The intermediate long-chain organomercury(II) acetates were obtained by condensation of 4-aminophenylmercury(II) acetate with the appropriate 4-n-alkoxybenzaldehydes. The thermal behaviour of the complexes was studied by polarized optical microscopy and differential scanning calorimetry but revealed no mesophases. All of the complexes, however, were reversibly photochromic (yellow ⇌ blue) upon irradiation of chloroform solutions with visible light, and the half-lives of the metastable blue forms were substantially increased relative to that of the parent mercury(II) bis(dithizonate). The compounds were not photochromic in the solid state. Copyright © 2000 John Wiley & Sons, Ltd.

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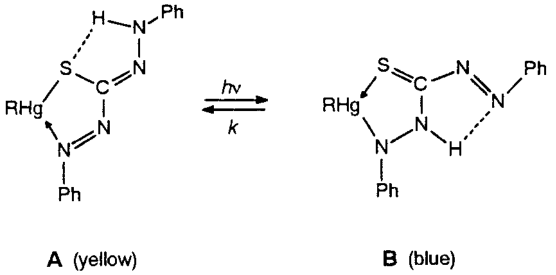
INTRODUCTION

Dithizone [1,5-diphenylthiocarbazone, PhN═N—C(SH)═N—NHPh ⇌ PhN═N—C(S)—NH—NHPh, abbreviated here as H_2dptc] forms strongly coloured complexes with many heavy metals and has extensive applications in analytical chemistry.[1–3] Irradiation by visible light of solutions of mercury(II) bis(dithizonate) [Scheme 1: **A**, R = Hdptc; IUPAC nomenclature: bis(1,5-diphenylthiocarbazonato-*N,S*)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 [$Hg(Hdptc)_2$] was first reported 50 years ago,[4–6] it was not until 1965 that Meriwether *et al.*[7,8] 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 1 min), the rates of the thermal return reactions (blue → yellow) were too fast for conventional measurements. From kinetic studies they proposed[8] the equilibrium shown in Scheme 1 (**A** ⇌ **B**, R = Hdptc), where the structure of only one of the ligands is shown in detail (both ligands photoisomerize).



Scheme 1

More recently, we showed that the yellow ⇌ blue photochromism persists in the *organo*mercury(II) dithizonates [RHg(Hdptc)] (Scheme 1, R = Me or Ph), where only one dithizonate ligand is present,[9,10] and we confirmed the structure of the

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stable yellow form of these 1:1 organomercury(II) complexes as **A** in Scheme 1, by X-ray diffraction.[11] In both of these structures the mercury atom exhibits planar, irregular three-coordination, the geometry at the mercury atom being approximately T-shaped. The characterization of these 1:1 organomercury(II) complexes of dithizone as photochromic compounds presented the opportunity for synthesizing further organomercury(II) dithizonates, it was to be hoped without inhibiting the well-established photochromism of the —Hg(Hdptc) moiety. We chose to examine a series of long-chain azomethine derivatives, thus building on and extending the phenylmercury(II) core structure. We report here on the synthetic strategy that was followed to prepare this series of 4-(4′-n-alkoxybenzylideneimino)phenylmercury(II) dithizonates, together with the spectroscopic characterization of the new compounds and their thermal and photochromic properties.

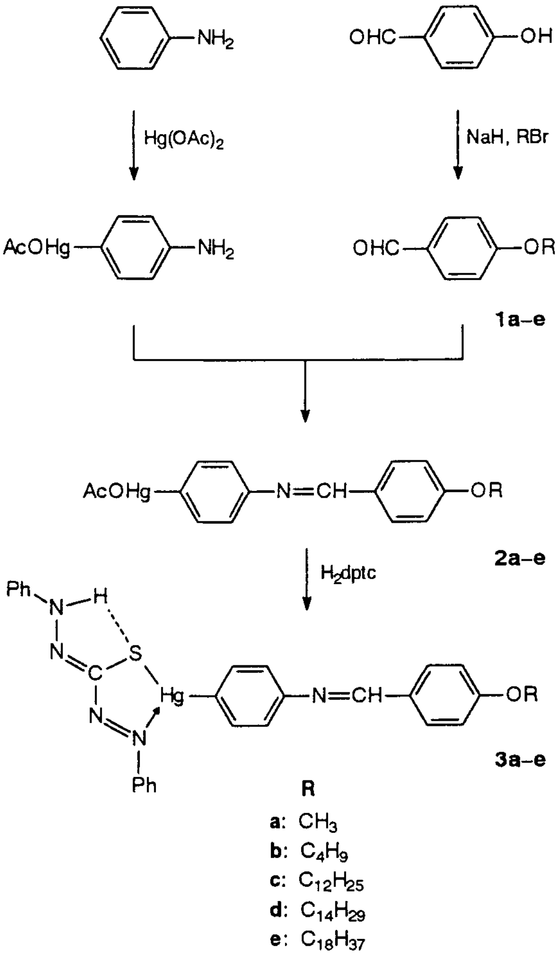
This work is of practical importance because of possible applications in optical recording and display devices,[12] and the suitability of the parent bis-dithizonate complex [Hg(Hdptc)$_2$] as a reusable optical recording medium for use in data processing applications has already been established.[13]

RESULTS AND DISCUSSION

Synthesis and characterization

The most direct route to compounds containing the azomethine linkage is the condensation of an aldehyde with a primary amine.[14] The synthetic route chosen was therefore the convergent one outlined in Scheme 2, in which the mercury atom was first introduced into the amine and the latter then condensed with a *para*-substituted n-alkoxybenzaldehyde (**1**) to give the Schiff-base derivative (**2**). The final step in Scheme 2 describes the coordination of dithizone to give the required long-chain organomercury(II) dithizonate (**3**).

4-Aminophenylmercury(II) acetate was prepared from aniline ($C_6H_5NH_2$) and mercury(II) acetate according to published methods.[15,16] The pure *para* isomer was isolated by filtration after a reaction time of 3 h and was obtained in considerably higher yield than that reported in the original literature (83% compared with 57%).[15] The product was of only limited solubility in most solvents and attempts at recrystallization were unsuccessful. However, ^{1}H NMR spectroscopy revealed a satisfactorily pure compound and this product was therefore taken straight through to the second step of the synthesis, i.e. condensation with the 4-n-alkoxybenzaldehydes (**1a**–**1e**).



Scheme 2

Interestingly, the melting point of 4-aminophenylmercury(II) acetate has been variously reported in the literature: the original paper by Dimroth[15] gives a value of 166–167 °C and this is misquoted in *Houben-Weyl*[16] as 67 °C, whereas more recent work[17] gives 148 °C. The melting point of the product obtained in this study was 158–160 °C, exactly the temperature range reported by Dimroth[15] for the *ortho* compound, which he found to be precipitated in low yield from the filtrate on standing. However, the product isolated here was unambiguously established as the *para* isomer by ^{1}H NMR spectroscopy, which clearly showed the signals characteristic of a *para*-disubstituted benzene ring, i.e. a set of two doublets with a coupling constant *J* of 8.5 Hz. A small amount of material was isolated from the filtrate but NMR spectroscopy again showed this to be the *para* isomer, with a melting point of 155–158 °C. A melting point for the *ortho* compound was therefore not obtained in this work, but the value of 166–167 °C is suggested if it is assumed that the melting points of the *ortho* and *para* isomers were inadvertently interchanged in the original paper and that this error has been perpetuated in the review literature.

Initial attempts to prepare those 4-n-alkoxybenzaldehydes that were not commercially available (**1c**–**1e**), by refluxing a solution of the n-alkyl bromide and 4-hydroxybenzaldehyde in cyclohexane with anhydrous potassium carbonate,[18] resulted in unacceptably low yields (*ca* 25%). It appeared to be necessary to use a stronger base and so the reaction using sodium hydride in *N*,*N*-dimethylformamide was investigated.[19] The reaction was complete within 1–2 h at elevated temperatures (100–110 °C) and gave good yields (82–89%) of **1c**–**1e** as waxy solids. We found that the low-melting products could be precipitated from solution by the addition of hexane, thus avoiding the need for distillation of these very high-boiling compounds.

Preparation of the Schiff-base mercury(II) acetates (**2a**–**2e**) was first attempted according to standard condensation procedures.[14,20] However, reaction of 4-methoxybenzaldehyde **1a** with 4-aminophenylmercury(II) acetate, in either refluxing toluene or refluxing benzene, gave no product and the amine remained in suspension unchanged. The extreme insolubility of the mercury salt in these and most other organic solvents thus appeared to inhibit the condensation. Consequently, it was decided to investigate the possibility of a reaction in the solid state. The 4-methoxybenzaldehyde **1a** was accordingly intimately mixed with a finely powdered sample of 4-aminophenylmercury(II) acetate and then heated at 150 °C. A pale yellow colour was immediately noticed as the amine appeared to melt, water vapour condensed at the mouth of the flask, and after less than 2 min at 150 °C the mixture abruptly solidified and heating was discontinued. The solid product was recrystallized from dichloromethane and identified as the required Schiff base **2a** by ^{1}H NMR spectroscopy. This procedure proved suitable for the small-scale preparation (*ca* 1 g) of all of the imines **2a–2e**, which were obtained in yields of 75–88%.

The ^{1}H NMR spectra of the compounds **2a–2e** (see the Experimental section) show the typical resonances expected for two *para*-disubstituted benzene rings; the assignments were confirmed by two-dimensional (2D) COSY experiments. The resonance for the azomethine proton in these compounds appeared in the range δ 8.26–8.37 ppm and, interestingly, in the case of **2a** a small signal, representing some 28% of the larger resonance at 8.26 ppm, was observed at 8.37 ppm. This was assumed to arise from the azomethine proton of the less-favoured *cis* isomer, which was expected to be present in only small amounts. For the longer-chain homologues **2b–2e** this peak was barely visible and these products were therefore assumed to be virtually pure *trans* isomers.

Finally, the 4-(4′-n-alkoxybenzylideneimino)-phenylmercury(II) dithizonates **3a–3e** were prepared following literature methods for related complexes,[10,21] in which stoichiometric ratios of the imines **2** and dithizone were stirred together in a 1-M aqueous ammonia–chloroform extraction system for 15 min. The resulting organomercury dithizonates were isolated from the bright red organic phase and were recrystallized from benzene–hexane to give dark red, microcrystalline solids, with yields typically in the range 55–70%.

Full characterizing data are given in the Experimental section. Assignment of the aromatic ^{1}H and ^{13}C NMR resonances of the dithizonato moiety was achieved by comparison with the NMR spectra of ethylmercury(II) dithizonate, [$CH_3CH_2Hg(Hdptc)$], in which the only aromatic signals are those arising from the dithizonato ligand. Assignment of the resonances due to the *ortho* protons of the phenyl ring attached to the imino group in [$CH_3CH_2Hg(Hdptc)$] was based on a weak coupling of these protons to the imino hydrogen that was observed in a 2D COSY experiment, and the remainder of the assignments then followed from a careful correlation of the cross-peaks in the COSY spectrum.

Thermal behaviour

Because of the rod-like shape of the long hydrocarbon chain and the high anisotropy of polarizability of the azomethine group, there is potential in these compounds to display the liquid-crystalline properties of a calamitic metallomesogen.[22] Indeed, the combination of the two phenomena of photochromism and liquid crystallinity in a single compound is an appealing goal. In the event, none of the dithizonate complexes **3a–3e** exhibited any liquid-crystalline behaviour. Instead, polarized optical microscopy and DSC thermograms indicated a sharp transition from the solid crystal to the isotropic melt, reproducible on repeated heating and cooling, and manifesting the expected trend of decreasing melting point with increasing length of the alkoxy chain.

The lack of any mesomorphic behaviour in the organomercury(II) dithizonates **3a–3e** can probably be attributed to the geometry of the dithizonato ligand, the shape and bulk of which might well be sufficient to overcome any tendency of the long-chain 4-(4′-n-alkoxybenzylideneimino)phenylmercury(II) system to form the parallel arrangement of molecules which exists in and defines the calamitic liquid-crystalline state.[22]

The corresponding precursor organomercury(II) acetates **2a–2e**, on the other hand, not possessing the bulky dithizonato ligand, might be expected to give rise to liquid-crystalline phases. Indeed, in his 1923 study of the first-ever reported metallomesogens, the bis[4-(4′-alkylbenzylideneimino)phenyl]-mercury(II) compounds, Vorländer[23] recorded a liquid-crystalline phase for the singly ligated 4-(4′-methoxybenzylideneimino)phenylmercury(II) acetate **2a** which was bounded by a melting point of 176 or 177 °C and a clearing point of 180 °C. In our hands, however, although a weakly birefringent phase of indeterminate texture was observed optically in this temperature range for the same compound prepared in this work (**2a**), separate peaks corresponding to crystal → mesophase and mesophase → isotropic liquid transitions were not detected in the DSC thermogram.

We obtained similar results for the other organomercury(II) acetates **2b–2e**. However, it is often difficult to distinguish between real and apparent birefringence[24] and in the case of the compounds **2b–2e** an apparently birefringent texture proved on closer examination to be simply unmelted crystallites in an otherwise isotropic environment. Again, no peaks corresponding to transitions to or from a mesophase were observed in the DSC thermograms.

Photochromic behaviour

The long-chain organomercury(II) dithizonates **3a–3e** exhibited similar photochromic behaviour to that observed for the parent compound, mercury(II) bis(dithizonate),[4–8] i.e. a reversible colour change from yellow to blue on irradiation with visible light of solutions of these compounds in organic solvents. The visible absorption spectra of chloroform solutions of these compounds were recorded in the range 400–700 nm; the spectra of the metastable blue forms were obtained by irradiating the sample in the quartz optical cell and then rapidly scanning the region of interest repeatedly in order to monitor the return reaction. The results are collected in Table 1 and typical spectra are reproduced in Fig. 1, where the single isosbestic

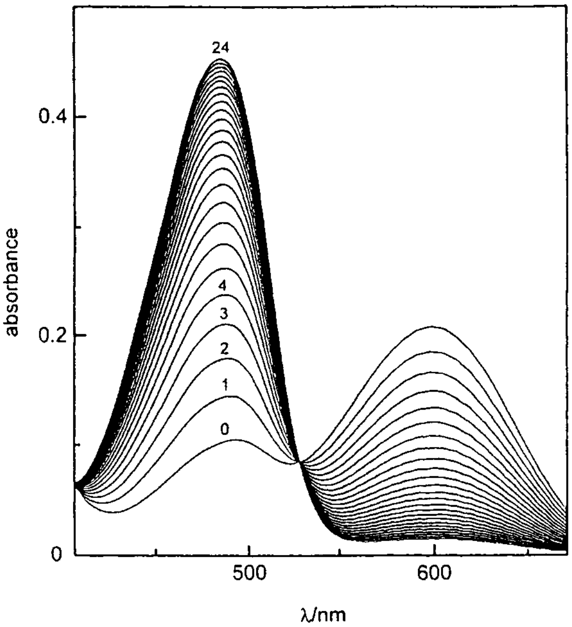


Figure 1 Visible absorption spectra of return reaction after irradiation of **3c** (1.05×10^{-5} M in dry $CHCl_3$). Spectra were run at 1-min intervals; the numbers on selected curves indicate the time in minutes after starting the first scan.

Table 1 Visible absorption spectral data for normal yellow and photoactivated blue forms of **3a–3e**

		λ_{max} (nm)[a]	
Complex	$t_{\frac{1}{2}}$ (min)[b]	Yellow form	Blue form
3a	3	485 (3550)	596
3b	3	484 (3950)	596
3c	5	487 (4400)	597
3d	5	486 (3850)	597
3e	6	487 (4200)	597

[a] Measured in $CHCl_3$ solution, *ca* 10^{-5} M. The absorption coefficient ($m^2\,mol^{-1}$) is given in parentheses for the yellow form only.

[b] Half-life of the labile blue form: estimated from several measurements and strongly sensitive to traces of water and other contaminants (see text). The error associated with these estimates is *ca* 1 min.

point between the absorption maxima of the normal and photoactivated forms indicates the absence of reaction intermediates or side reactions.

The visible absorption maxima of both the yellow and blue forms proved to be essentially independent of the nature of the long-chain organic ligand, a result consistent with the observations already made that the transitions involved are primarily associated with the delocalized electronic system of the dithizonato ligand and that replacement of one of the two dithizonato moieties of the mercury(II) bis(dithizonate) by an alkyl or aryl group does not significantly alter the behaviour of the remaining one.[9,10] It is interesting to note that the absorption coefficients for the yellow forms of the organomercury(II) complexes **3a–3e** in chloroform (Table 1) are virtually half of that found for the bis complex [Hg(Hdptc)$_2$] in chloroform ($\varepsilon = 7050\ \mathrm{m}^2\ \mathrm{mol}^{-1}$),[10] where, of course, there are two identical absorbing chromophores. The absorption coefficients for the blue forms were not obtained because of the difficulty of maintaining a steady-state concentration of 100% of the photoactivated form. However, an estimate of *ca* $1700\ \mathrm{m}^2\ \mathrm{mol}^{-1}$ for the blue forms of the 1:1 organomercury(II) dithizonates reported here is reasonable in view of the values 3900 and $2700\ \mathrm{m}^2\ \mathrm{mol}^{-1}$ reported for the blue form of the 1:2 mercury(II) bis(dithizonate) in benzene.[8,25]

While the half-life of the labile blue form of the parent mercury(II) bis(dithizonate) in chloroform is of the order of 1 min,[7,8,25] the same parameter for the organomercury(II) dithizonates **3a–3e** was consistently increased. Difficulty was encountered in obtaining reproducible thermal return rates for these compounds, but a qualitative study indicated that the half-lives increased with increasing chain length of the alkoxy substituent: a maximum value of *ca* 6 min was recorded for the compound **3e**. The notorious sensitivity of the photochromic mercury(II)–dithizonate system to the smallest traces of water or other contaminants in the organic solvent (or even adsorbed on the surfaces of the optical cells)[8,10,21] accounts for the poor reproducibility observed for the thermal return rates.

The compounds **3a–3e** were investigated for photochromism in the solid state: samples were separately smeared onto glass slides and irradiated through IR- and UV-absorbing filters. The materials all appeared to deteriorate on continued exposure: a degree of darkening was observed after 1 h and this increased with time, but no orange → violet colour change was observed as was reported for the mercury(II) bis(dithizonate)[7] and the experiment was discontinued after 6 h. The photochromism therefore does not appear to proceed at a measurable rate in the absence of a solvent.

EXPERIMENTAL

General

All reagents used in the preparative work were analytically pure and mostly supplied by Aldrich, including the 4-alkoxybenzaldehydes **1a** and **1b**. Solvents were purified according to standard procedures. Thin-layer chromatography was performed on Merck silica gel 60 F_{254} aluminium-backed plates. ^{1}H NMR spectra were obtained at 200 MHz on a Varian VXR-200 spectrometer, while ^{13}C NMR spectra were obtained at 100 MHz on a Varian Unity-400 instrument. All NMR spectra were recorded as $CDCl_3$ solutions, chemical shifts are quoted relative to tetramethylsilane, and the coupling constants, *J*, are given in hertz. Microanalyses were obtained using a Carlo Erba EA-1108 elemental analyser.

Thermal behaviour was studied using a Nikon SMZ-10 optical microscope equipped with a polarizer and a Linkam CO-600 hot stage. In the experimental data for the preparative work that follows, where a single figure is quoted for a melting point, this is the onset temperature as determined from the DSC thermogram; otherwise, where a range is given, this is the melting point as determined using a Reichert–Jung Thermovar hot-stage microscope. DSC thermograms were recorded on a Perkin-Elmer DSC-7 instrument at heating and cooling rates of $10\ °\mathrm{C\ min}^{-1}$ and with a nitrogen flow rate of $40\ \mathrm{cm}^3\ \mathrm{min}^{-1}$. The instrument was calibrated with indium (156.6 °C, $28.45\ \mathrm{J\ g}^{-1}$) and zinc (419.47 °C, $108.37\ \mathrm{J\ g}^{-1}$).

Visible absorption spectra were recorded on a Philips PU-8720 UV–visible spectrophotometer using a 1-cm quartz optical cell. The light source used for irradiating the samples (either as chloroform solutions in optical cells or as solids smeared on glass slides) was an Osram 'Power Star' HQI-T 400 W metal halide lamp, generally used with IR- and UV-absorbing filters. This provided a broad spectrum of radiation in the visible region with a strong emission line at 514 nm. Visible spectra of the photoexcited blue forms were recorded by irradiating the sample (dissolved in purified and scrupulously dried chloroform, *ca* $10^{-5}\ \mathrm{mol\ dm}^{-3}$) in an 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. When attempts were being made to observe the activated blue form of the complexes special care was taken in cleaning (and drying) glassware and optical cells so as to remove traces of any impurities which might accelerate the return reaction.

Syntheses

4-Aminophenylmercury(II) acetate

Freshly distilled aniline ($C_6H_5NH_2$) (5.84 g, 62.7 mmol) was added to a solution of mercury(II) acetate (10.0 g, 31.4 mmol) in water (50 cm^3) and the reaction mixture was stirred at room temperature for a total of 3 h, during which time a white precipitate formed. This product was filtered off and air-dried to give 4-aminophenylmercury(II) acetate (9.21 g, 83%), m.p. 158–160 °C (Found: C, 27.0; H, 2.4; N, 3.9. Calc. for $C_8H_9HgNO_2$: C, 27.3; H, 2.6; N, 4.0%). ^{1}H NMR: $\delta_H = 2.08$ (3H, s, CH_3CO_2), 3.74 (2H, br s, NH_2), 6.69 (2H, d, $J = 8.5$, ArH) and 7.06 (2H, d, $J = 8.5$, ArH).

4-n-Alkoxybenzaldehydes (1c–1e)

In a typical procedure, sodium hydride (0.18 g, 6.14 mmol; an 80% dispersion in mineral oil) was added to a solution of 4-hydroxybenzaldehyde (0.50 g, 4.09 mmol) in freshly distilled *N*,*N*-dimethylformamide (10 cm^3) at room temperature. The addition was accompanied by vigorous effervescence and evolution of hydrogen; this exothermic reaction was allowed to subside slightly before addition of the appropriate alkyl bromide (4.91 mmol) in a single portion. The reaction flask was immediately placed in an oil bath preheated to 110–115 °C. The reaction mixture gradually lightened in colour from dark orange to pale yellow. The reaction was monitored by TLC (ethyl acetate–toluene, 70:30) for the complete disappearance of the 4-hydroxybenzaldehyde and was complete after 1½–2 h. The mixture was allowed to cool slightly and the product was precipitated from solution by the addition of hexane. This solid material was filtered, washed with hexane and air-dried to yield the products **1c–1e** (^{1}H and ^{13}C NMR assignments for the aromatic hydrogen and carbon atoms are referenced to the IUPAC numbering convention for a substituted benzaldehyde).

*4-Dodecyloxybenzaldehyde (***1c***)*

Yield 0.98 g, 82%; m.p. 20–23 °C (lit.,[18] 24 °C) (Found: C, 78.5; H, 10.3. Calc. for $C_{19}H_{30}O_2$: C, 78.6; H, 10.4%). ^{1}H NMR: $\delta_H = 0.88$ (3H, t, CH_3), 1.27 [18H, m, $(CH_2)_9$], 1.81 (2H, quintet, OCH_2CH_2), 4.04 (2H, t, OCH_2), 6.99 (2H, d, $J_{3,2} = 8.7$, ArH^3), 7.82 (2H, d, $J_{2,3} = 8.8$, ArH^2) and 9.87 (1H, s, CHO). ^{13}C NMR: $\delta_C = 14.01$ (CH_3), 22.67 (CH_3CH_2), 25.99 ($CH_3CH_2CH_2$), 29.07–29.66 [$(CH_2)_7$], 31.94 (OCH_2CH_2), 68.39 (OCH_2), 114.77 (ArC^3), 129.73 (ArC^1), 131.95 (ArC^2), 164.30 (ArC^4) and 190.78 (CHO).

*4-Tetradecyloxybenzaldehyde (***1d***)*

Yield 1.16 g, 89%; m.p. 33–34 °C (lit.,[18] 34 °C) (Found: C, 79.0; H, 10.6. Calc. for $C_{21}H_{34}O_2$: C, 79.2; H, 10.75%). ^{1}H NMR: $\delta_H = 0.88$ (3H, t, CH_3), 1.26 [22H, m, $(CH_2)_{11}$], 1.81 (2H, quintet, OCH_2CH_2), 4.04 (2H, t, OCH_2), 6.98 (2H, d, $J_{3,2} = 8.8$, ArH^3), 7.82 (2H, d, $J_{2,3} = 8.8$, ArH^2) and 9.87 (1H, s, CHO). ^{13}C NMR: $\delta_C = 14.07$ (CH_3), 22.66 (CH_3CH_2), 25.93 ($CH_3CH_2CH_2$), 29.03–29.62 [$(CH_2)_9$], 31.89 (OCH_2CH_2), 68.41 (OCH_2), 114.73 (ArC^3), 129.73 (ArC^1), 131.94 (ArC^2), 164.26 (ArC^4) and 190.74 (CHO).

*4-Octadecyloxybenzaldehyde (***1e***)*

Yield 1.36 g, 89%; m.p. 45–48 °C (lit.,[18] 49 °C) (Found: C, 79.9; H, 11.1. Calc. for $C_{25}H_{42}O_2$: C, 80.2; H, 11.3%). ^{1}H NMR: $\delta_H = 0.88$ (3H, t, CH_3), 1.26 [30H, m, $(CH_2)_{15}$], 1.81 (2H, quintet, OCH_2CH_2), 4.04 (2H, t, OCH_2), 6.99 (2H, d, $J_{3,2} = 8.7$, ArH^3), 7.82 (2H, d, $J_{2,3} = 8.8$, ArH^2) and 9.87 (1H, s, CHO). ^{13}C NMR: $\delta_C = 13.98$ (CH_3), 22.57 (CH_3CH_2), 25.84 ($CH_3CH_2CH_2$), 29.23–29.57 [$(CH_2)_{13}$], 31.81 (OCH_2CH_2), 68.33 (OCH_2), 114.65 (ArC^3), 129.64 (ArC^1), 131.85 (ArC^2), 164.18 (ArC^4) and 190.68 (CHO).

4-(4′-n-Alkoxybenzylideneimino)-phenylmercury(II) acetates (2a–2e)

In a typical procedure, a finely powdered sample of 4-aminophenylmercury(II) acetate (1.00 g, 2.84 mmol) was placed in a small round-bottomed flask and the appropriate 4-n-alkoxybenzaldehyde (2.84 mmol) was added. The two reagents were intimately mixed and the open reaction flask was then placed in an oil bath preheated to 150–155 °C. A yellow colour was immediately evident as the mixture began to liquefy. Water vapour was evolved and condensed at the mouth of the flask. After no more than 2–3 min of heating at an oil-bath temperature of 150–155 °C, the mixture abruptly solidified; the flask was then removed from the heat and the condensate removed from the mouth of the flask by touching a small piece of tissue to the droplets. The solid material was recrystallized from dichloromethane to give micro-

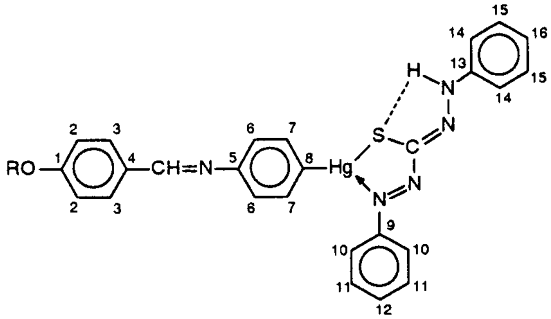


Figure 2 Numbering system for NMR assignments of aromatic hydrogen and carbon atoms in **3a–3e**, **2a–2e** (where an acetato ligand replaces the indicated dithizonato moiety) and ethylmercury(II) dithizonate [where an ethyl group replaces the indicated 4-(4′-n-alkoxybenzylideneimino)phenyl group].

crystalline powders of the products **2a–2e** (^{1}H and ^{13}C NMR assignments for the aromatic hydrogen and carbon atoms are referenced to the arbitrary numbering scheme depicted in Fig. 2).

*4-(4′-Methoxybenzylideneimino)phenylmercury(II) acetate (***2a***)*

Yield 1.18 g, 88%; m.p. 176 °C (Found: C, 40.75; H, 3.1; N, 3.0. $C_{16}H_{15}HgNO_3$ requires C, 40.9; H, 3.2; N, 3.0%). ^{1}H NMR: $\delta_H = 2.02$ (3H, s, CH_3CO_2), 3.80 (3H, s, CH_3O), 6.91 (2H, d, $J_{2,3} = 8.8$, H^2), 7.12 (2H, d, $J = 8.6$, H^6 or H^7), 7.24 (2H, d, $J = 8.6$, H^7 or H^6), 7.77 (2H, d, $J_{3,2} = 8.8$, H^3), 8.26 (0.78H, s, CH=N, *trans* isomer) and 8.37 (0.22H, s, CH=N, *cis* isomer).

*4-(4′-Butoxybenzylideneimino)phenylmercury(II) acetate (***2b***)*

Yield 1.25 g, 86%; m.p. 186 °C (Found: C, 44.3; H, 3.9; N, 2.7. $C_{19}H_{21}HgNO_3$ requires C, 44.6; H, 4.1; N, 2.7%). ^{1}H NMR: $\delta_H = 0.92$ (3H, t, CH_3), 1.44 (2H, sextet, CH_3CH_2), 1.74 (2H, quintet, $CH_3CH_2CH_2$), 2.03 (3H, s, CH_3CO_2), 3.96 (2H, t, OCH_2), 6.90 (2H, d, $J_{2,3} = 8.8$, H^2), 7.12 (2H, d, $J = 8.5$, H^6 or H^7), 7.25 (2H, d, $J = 8.5$, H^7 or H^6), 7.76 (2H, d, $J_{3,2} = 8.8$, H^3), 8.26 (0.9H, s, CH=N, *trans* isomer) and 8.37 (0.1H, s, CH=N, *cis* isomer).

*4-(4′-Dodecyloxybenzylideneimino)-phenylmercury(II) acetate (***2c***)*

Yield 1.50 g, 85%; m.p. 183 °C (Found: C, 51.7; H, 5.95; N, 2.1. $C_{27}H_{37}HgNO_3$ requires C, 51.95; H, 6.0; N, 2.2%). ^{1}H NMR: $\delta_H = 0.88$ (3H, t, CH_3), 1.27 [18H, m, $(CH_2)_9$], 1.81 (2H, quintet, OCH_2CH_2), 2.10 (3H, s, CH_3CO_2), 4.02 (2H, t, OCH_2), 6.97 (2H, d, $J_{2,3} = 8.8$, H^2), 7.19 (2H, d, $J = 8.5$, H^6 or H^7), 7.32 (2H, d, $J = 8.5$, H^7 or H^6), 7.83 (2H, d, $J_{3,2} = 8.7$, H^3) and 8.33 (1H, s, CH=N). ^{13}C NMR: $\delta_C = 14.09$ (CH_3), 22.67 (CH_3CH_2), 23.18 (CH_3CO_2), 25.99 ($CH_3CH_2CH_2$), 29.15–29.62 [$(CH_2)_7$], 31.90 (OCH_2CH_2), 68.24 (OCH_2), 114.73 (C^2), 121.54 (C^6 or C^7), 128.76 (C^4), 130.65 (C^3), 136.77 (C^7 or C^6), 153.45 (C^5 or C^8), 160.49 (CH=N), 162.12 (C^1) and 177.58 (C^8 or C^5).

*4-(4′-Tetradecyloxybenzylideneimino)-phenylmercury(II) acetate (***2d***)*

Yield 1.54 g, 83%; m.p. 151 °C (Found: C, 53.25; H, 6.1; N, 2.0. $C_{29}H_{41}HgNO_3$ requires C, 53.4; H, 6.3; N, 2.15%). ^{1}H NMR: $\delta_H = 0.86$ (3H, t, CH_3), 1.24 [22H, m, $(CH_2)_{11}$], 1.79 (2H, quintet, OCH_2CH_2), 2.10 (3H, s, CH_3CO_2), 4.00 (2H, t, OCH_2), 6.95 (2H, d, $J_{2,3} = 8.8$, H^2), 7.18 (2H, d, $J = 8.5$, H^6 or H^7), 7.30 (2H, d, $J = 8.5$, H^7 or H^6), 7.81 (2H, d, $J_{3,2} = 8.8$, H^3) and 8.32 (1H, s, CH=N).

*4-(4′-Octadecyloxybenzylideneimino)-phenylmercury(II) acetate (***2e***)*

Yield 1.34 g, 67%; m.p. 119 °C (Found: C, 55.7; H, 6.8; N, 1.9. $C_{33}H_{49}HgNO_3$ requires C, 55.95; H, 7.0; N, 2.0%). ^{1}H NMR: $\delta_H = 0.87$ (3H, t, CH_3), 1.26 [30H, m, $(CH_2)_{15}$], 1.81 (2H, quintet, OCH_2CH_2), 2.10 (3H, s, CH_3CO_2), 4.02 (2H, t, OCH_2), 6.97 (2H, d, $J_{2,3} = 8.8$, H^2), 7.20 (2H, d, $J = 8.5$, H^6 or H^7), 7.32 (2H, d, $J = 8.5$, H^7 or H^6), 7.83 (2H, d, $J_{3,2} = 8.8$, H^3) and 8.34 (1H, s, CH=N). ^{13}C NMR: $\delta_C = 14.10$ (CH_3), 22.68 (CH_3CH_2), 23.13 (CH_3CO_2), 26.00 ($CH_3CH_2CH_2$), 29.16–29.68 [$(CH_2)_{13}$], 31.91 (OCH_2CH_2), 68.24 (OCH_2), 114.73 (C^2), 121.55 (C^6 or C^7), 128.76 (C^4), 130.66 (C^3), 136.76 (C^7 or C^6), 153.45 (C^5 or C^8), 160.52 (CH=N), 162.10 (C^1) and 177.60 (C^8 or C^5).

4-(4′-n-Alkoxybenzylideneimino)-phenylmercury(II) dithizonates (3a–3e)

In a typical procedure, the appropriate 4-(4′-n-alkoxybenzylideneimino)phenylmercury(II) acetate **2** (1.1 g) and analytical-grade dithizone (1 mol equiv) were separately dissolved in dichloromethane (50 cm^3 each) and then shaken together at room temperature for 15 min with a 1-M aqueous ammonia solution (100 cm^3). A bright red colour was immediately obtained in the organic phase. The two phases were separated and the organic layer was washed first with water (100 cm^3), then with 1-M aqueous sodium hydroxide (100 cm^3) and finally again with water (100 cm^3). The aqueous washings were a pale yellow colour and were discarded. The combined organic phases were dried over magnesium sulfate, filtered and evaporated to dryness. The residue was recrystallized from benzene–hexane to yield deep red microcrystalline powders of the products **3a–3e** (^{1}H and ^{13}C NMR assignments for the aromatic hydrogen and carbon atoms are referenced to the arbitrary numbering scheme depicted in Fig. 2).

*4-(4′-Methoxybenzylideneimino)phenylmercury(II) dithizonate (**3a**)*

Yield 0.97 g, 62%; m.p. 189 °C (Found: C, 48.5; H, 3.25; N, 10.3. $C_{27}H_{23}HgN_5OS$ requires C, 48.7; H, 3.5; N, 10.5%). ^{1}H NMR: $\delta_H = 3.89$ (3H, s, CH_3O), 7.00 (2H, d, $J_{2,3} = 8.9$, H^2), 7.07 (1H, m, H^{16}), 7.28 (H^6 or H^7, obscured by residual $CHCl_3$), 7.44 (9H, m, H^{11}, H^{12}, H^{14}, H^{15} and H^7 or H^6), 7.88 (2H, d, $J_{3,2} = 8.8$, H^3), 7.96 (2H, m, H^{10}), 8.43 (1H, s, CH═N) and 9.23 (1H, br s, NH). ^{13}C NMR: $\delta_C = 55.45$ (CH_3O), 114.25 (C^2), 115.18 (C^{14} or C^{15}), 121.43 (C^6 or C^7), 123.03 (C^{10} or C^{16}), 123.34 (C^{16} or C^{10}), 129.37 (C^{11} or C^{14} or C^{15}), 129.44 (C^{11} or C^{14} or C^{15}), 130.60 (C^3 or C^{12}), 130.76 (C^{12} or C^3), 137.39 (C^7 or C^6), 142.18 (C^9 or C^{13}), 151.41 (C^{13} or C^9), 152.39 (C^5 or C^8) and 159.79 (CH═N).

*4-(4′-Butoxybenzylideneimino)phenylmercury(II) dithizonate (**3b**)*

Yield 0.90 g, 59%; m.p. 176 °C (Found: C, 50.5; H, 3.8; N, 9.7. $C_{30}H_{29}HgN_5OS$ requires C, 50.9; H, 4.1; N, 9.9%). ^{1}H NMR: $\delta_H = 1.00$ (3H, t, CH_3), 1.54 (2H, sextet, $CH_3C\mathit{H}_2$), 1.81 (2H, quintet, $OCH_2C\mathit{H}_2$), 4.04 (2H, t, OCH_2), 6.98 (2H, d, $J_{2,3} = 8.8$, H^2), 7.07 (1H, m, H^{16}), 7.26 (2H, d, $J = 8.4$, H^6 or H^7), 7.40 (7H, m, H^{11}, H^{12}, H^{14} and H^{15}), 7.47 (2H, d, $J = 8.4$, H^7 or H^6), 7.85 (2H, d, $J_{3,2} = 8.8$, H^3), 7.94 (2H, m, H^{10}), 8.39 (1H, s, CH═N) and 9.20 (1H, s, NH). ^{13}C NMR: $\delta_C =$ 13.83 (CH_3), 19.22 ($CH_3\mathit{C}H_2$), 31.21 ($OCH_2\mathit{C}H_2$), 67.90 (OCH_2), 114.71 (C^2), 115.16 (C^{14} or C^{15}), 121.43 (C^6 or C^7), 123.02 (C^{10} or C^{16}), 123.31 (C^{16} or C^{10}), 128.95 (C^4), 129.34 (C^{14} or C^{15} or C^{16}), 129.42 (C^{14} or C^{15} or C^{16}), 130.57 (C^3 or C^{12}), 130.73 (C^{12} or C^3), 137.41 (C^7 or C^6), 142.14 (C^9 or C^{13}), 151.45 (C^{13} or C^9), 152.39 (C^5 or C^8), 160.01 (CH═N), 162.01 (C^1) and 177.60 (C^8 or C^5).

*4-(4′-Dodecyloxybenzylideneimino)-phenylmercury(II) dithizonate (**3c**)*

Yield 0.98 g, 68%; m.p. 151 °C (Found: C, 55.2; H, 5.2; N, 8.3. $C_{38}H_{45}HgN_5OS$ requires C, 55.6; H, 5.5; N, 8.5%). ^{1}H NMR: $\delta_H = 0.89$ (3H, t, CH_3), 1.28 [16H, m, $(CH_2)_8$], 1.48 (2H, m, $OCH_2CH_2C\mathit{H}_2$), 1.81 (2H, quintet, $OCH_2C\mathit{H}_2$), 4.03 (2H, t, OCH_2), 6.99 (2H, d, $J_{2,3} = 8.8$, H^2), 7.07 (1H, m, H^{16}), 7.26 (2H, d, $J = 8.0$, H^6 or H^7), 7.39 (7H, m, H^{11}, H^{12}, H^{14} and H^{15}), 7.48 (2H, d, $J = 8.0$, H^7 or H^6), 7.85 (2H, d, $J_{3,2} = 8.8$, H^3), 7.96 (2H, m, H^{10}), 8.41 (1H, s, CH═N) and 9.21 (1H, s, NH). ^{13}C NMR: $\delta_C = 14.11$ (CH_3), 22.68 ($CH_3\mathit{C}H_2$), 26.01 ($CH_3CH_2\mathit{C}H_2$), 29.18–29.64 [$(CH_2)_7$], 31.91 ($OCH_2\mathit{C}H_2$), 68.25 (OCH_2), 114.75 (C^2), 115.16 (C^{14} or C^{15}), 121.44 (C^6 or C^7), 123.04 (C^{10} or C^{16}), 123.33 (C^{16} or C^{10}), 128.96 (C^4), 129.37 (C^{14} or C^{15} or C^{16}), 129.44 (C^{14} or C^{15} or C^{16}), 130.59 (C^3 or C^{12}), 130.76 (C^{12} or C^3), 137.39 (C^7 or C^6), 142.18 (C^9 or C^{13}), 151.40 (C^{13} or C^9), 152.43 (C^5 or C^8), 160.05 (CH═N), 162.03 (C^1) and 177.60 (C^8 or C^5).

*4-(4′-Tetradecyloxybenzylideneimino)-phenylmercury(II) dithizonate (**3d**)*

Yield 0.80 g, 56%; m.p. 129 °C (Found: C, 56.3; H, 5.7; N, 8.1. $C_{40}H_{49}HgN_5OS$ requires C, 56.6; H, 5.8; N, 8.25%). ^{1}H NMR: $\delta_H = 0.89$ (3H, t, CH_3), 1.27 [22H, m, $(CH_2)_{11}$], 1.81 (2H, quintet, $OCH_2C\mathit{H}_2$), 4.03 (2H, t, OCH_2), 6.99 (2H, d, $J_{2,3} = 8.8$, H^2), 7.07 (1H, m, H^{16}), 7.28 (H^6 or H^7, obscured by residual $CHCl_3$), 7.44 (9H, m, H^{11}, H^{12}, H^{14}, H^{15} and H^7 or H^6), 7.86 (2H, d, $J_{3,2} = 8.8$, H^3), 7.95 (2H, m, H^{10}), 8.42 (1H, s, CH═N) and 9.22 (1H, br s, NH).

*4-(4′-Octadecyloxybenzylideneimino)-phenylmercury(II) dithizonate (**3e**)*

Yield 0.70 g, 50%; m.p. 123 °C (Found: C, 58.25; H, 6.25; N, 7.6. $C_{44}H_{57}HgN_5OS$ requires C, 58.4; H, 6.35; N, 7.7%). ^{1}H NMR: $\delta_H = 0.87$ (3H, t, CH_3), 1.26 [30H, m, $(CH_2)_{15}$], 1.81 (2H, quintet, $OCH_2C\mathit{H}_2$), 4.02 (2H, t, OCH_2), 6.98 (2H, d, $J_{2,3} = 8.8$, H^2), 7.10 (1H, m, H^{16}), 7.28 (H^6 or H^7, obscured by residual $CHCl_3$), 7.44 (9H, m, H^{11}, H^{12}, H^{14}, H^{15} and H^7 or H^6), 7.86 (2H, d, $J_{3,2} = 8.8$, H^3), 7.94 (2H, m, H^{10}), 8.48 (1H, s, CH═N) and 9.21 (1H, br s, NH).

Ethylmercury(II) dithizonate

Solutions of ethylmercury(II) chloride (Johnson Matthey Alfa Products; 0.50 g, 1.89 mmol) and analytical-grade dithizone (0.48 g, 1.89 mmol) in dichloromethane (50 cm^3 each) were shaken together for 15 min with a 1-M aqueous ammonia solution (100 cm^3). The product was isolated from the organic phase following the procedure described above for the compounds **3a–3e** and was recrystallized from benzene–hexane to yield ethylmercury(II) dithizonate as a deep red microcrystalline powder (0.66 g, 73%), m.p. 157–159 °C (lit.,[6] 158–158.5 °C) (Found: C, 36.95; H, 3.2; N, 11.5. Calc. for $C_{15}H_{16}HgN_4S$: C, 37.15; H, 3.3; N, 11.55%). ^{1}H NMR: $\delta_H = 1.45$ (3H, t, CH_3), 1.93 (2H, q, $CH_3C\mathit{H}_2$), 7.03 (1H, m, H^{16}), 7.36 (4H, m, H^{14} and H^{15}), 7.43 (1H, m, H^{12}), 7.48 (2H, m, H^{11}), 7.89 (2H, m, H^{10}) and 9.17 (1H, s, NH). ^{13}C NMR: $\delta_C = 14.64$ (CH_3), 25.20 ($CH_3\mathit{C}H_2$), 115.09 (C^{14} or C^{15}), 122.82 (C^{10}), 123.04 (C^{16}), 129.39 (C^{11} or C^{14} or C^{15}), 129.40 (C^{11} or C^{14} or C^{15}), 130.59 (C^{12}), 142.29 (C^9 or C^{13}), 151.54 (C^{13} or C^9) and 155.58 (CS).

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