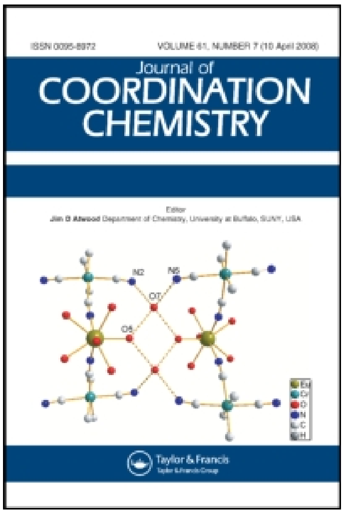

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PHOTOCHROMIC LONG-CHAIN ORGANOMERCURY(II) DITHIZONATE COMPLEXES IN THE BIPHENYL SERIES

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PHOTOCHROMIC LONG-CHAIN ORGANOMERCURY(II) DITHIZONATE COMPLEXES IN THE BIPHENYL SERIES

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The synthesis and characterization of a new series of 4-(4′-*n*-alkoxybiphenyl)mercury(II) dithizonates, [$C_nH_{2n+1}OC_6H_4C_6H_4Hg(Hdptc)$] ($H_2dptc$ = 1,5-diphenylthiocarbazone = dithizone; $n = 4$, 5, 10, 14 or 18), is described. Meticulous attention to reaction conditions was crucial for the successful synthesis of the intermediate long-chain 4-(4′-*n*-alkoxybiphenyl) mercury(II) bromides, which were obtained by room temperature reaction of the 4-alkoxy-4′-lithiobiphenyl derivatives with $HgBr_2$ in diethylether. A new, improved procedure was developed for the final dithizone complexation step. A study of the thermal behaviour of the complexes by polarized optical microscopy and differential scanning calorimetry revealed no mesophases. All of the complexes, however, were reversibly photochromic (yellow $\rightleftharpoons$ blue) upon irradiation of chloroform solutions with visible light, and the half-lives of the meta-stable blue forms were substantially increased relative to that of the parent mercury(II) bis(dithizonate).

Keywords: Photochromism; Organomercury; Long-chain; Biphenyl derivatives; 4-(4′-*n*-alkoxy-biphenyl)mercury(II); Dithizonate complexes

INTRODUCTION

The well-known analytical reagent dithizone [1,5-diphenylthiocarbazone, PhN=N—C(SH)=N—NHPh $\rightleftharpoons$ PhN=N—C(S)—NH—NHPh, abbreviated here as H_2dptc] forms strongly coloured complexes with many heavy metals [1-3]. Solutions in organic solvents of mercury(II) bis(dithizonate) [Scheme 1: **A**, R = Hdptc; IUPAC nomenclature:

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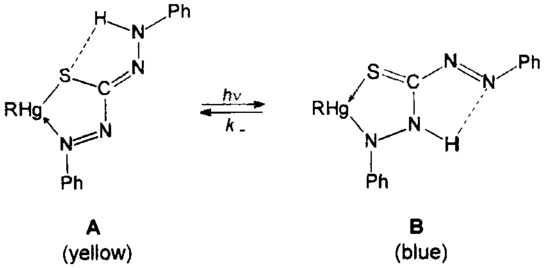
*Corresponding author. e-mail: athutton@psipsy.uct.ac.za bis(1,5-diphenylthiocarbazonato-*N*,*S*)mercury(II)], when irradiated with visible light, undergo a reversible colour change from yellow to blue, the normal form having a strong absorption band at 485 nm in chloroform which is replaced in the activated form by a band at 604 nm. The photochromic behaviour of [Hg(Hdptc)$_2$] was first reported more than fifty years ago [4–6], but the phenomenon was not studied in detail until 1965, when Meriwether *et al.* [7, 8] showed that photochromism was observable in all heavy metal dithizonates. However, 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 generally too fast for conventional spectroscopic measurements. The equilibrium shown in Scheme 1 (**A** $\rightleftharpoons$ **B**, R = Hdptc) was proposed from kinetic studies [8]; here it should be noted that although the structure of only one of the ligands is shown in detail, both ligands photoisomerize.



SCHEME 1

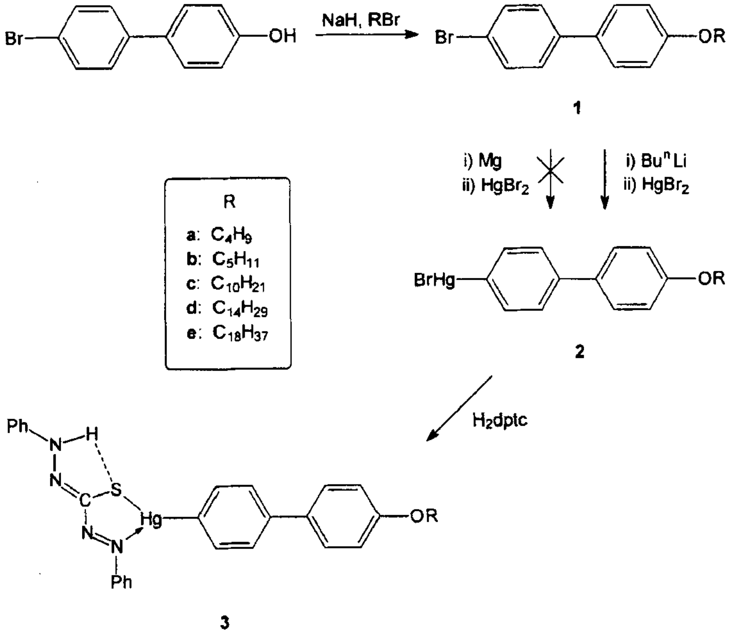
Our own work has shown that the yellow $\rightleftharpoons$ blue photochromism persists in the *organo*mercury(II) dithizonates [*R*Hg(Hdptc)] (Scheme 1, R = Me or Ph), where only one dithizonate ligand is present [9, 10], and we have confirmed by X-ray crystallography that the structure of the stable yellow form of these 1 : 1 organomercury(II) complexes is as **A** in Scheme 1 [11]. The geometry at the mercury atom is approximately *T*-shaped in both of these structures, the mercury atom exhibiting planar, irregular three-coordination. We have now elaborated on and extended this phenylmercury(II) core structure by synthesizing a series of long-chain alkoxybiphenyl derivatives in the hope that the well-established photochromism of the —Hg(Hdptc) moiety would not be inhibited. We report here on the synthetic strategy that was adopted to prepare this series of 4-(4′-*n*-alkoxybiphenyl)mercury(II) dithizonates, and provide details of the spectroscopic characterization of the new compounds together with their thermal and photochromic properties.

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 recognized [12], and thus the possible applications in optical recording and display devices give this work some practical importance [13].

RESULTS AND DISCUSSION

Synthesis and Characterization

Scheme 2 shows that the key step in the synthesis of the 4-(4′-*n*-alkoxybiphenyl)mercury(II) dithizonate complexes **3** is the introduction of a single mercury atom into the biphenyl nucleus of the alkoxybromobiphenyls **1** at a position *para* to the long alkoxy chain to give the organomercury bromides **2**. The bromide ion should then be readily displaced by coordination of dithizone to the organomercury(II) moiety to provide the required long-chain organomercury(II) dithizonates **3**.



SCHEME 2

4-n-Alkoxy-4′-bromobiphenyls (1a – e)

The first step, starting from the commercially available 4-bromo-4′-hydroxybiphenyl, was to protect the hydroxyl group as the ether, thus preventing reaction of magnesium or lithium at this site and, at the same time, conveniently introducing the desired long alkoxy chain. Thus the 4-*n*-alkoxy-4′-bromobiphenyls **1a – e** were prepared in high yield (80 – 90%) and purity by the Williamson ether synthesis [14], in which 4-bromo-4′-hydroxybiphenyl in DMF was reacted with sodium hydride followed by the appropriate alkyl bromide. Reaction was usually complete after 1 h at near-reflux temperature and the product was precipitated out of solution by pouring onto crushed ice and then isolated by filtration. This material was recrystallized from methanol to give a fine, white powder (**1a – b**) or from chloroform to give large, semi-translucent, white platelets (**1c – e**). The thermal behaviour of these 4-*n*-alkoxy-4′-bromobiphenyls proved interesting, showing both crystalline polymorphism (**1a – b**) and liquid-crystalline properties (**1c – e**). Full experimental details and characterizing data for these purely organic intermediates will therefore appear in a study devoted to their thermal properties [15].

4-(4′-n-Alkoxybiphenyl)mercury(II) Bromides (2a – e)

Reaction of the 4-*n*-alkoxy-4′-bromobiphenyls **1** with magnesium was expected to give the corresponding organomagnesium bromides. These Grignard reagents are not isolated and usually react smoothly with mercury(II) bromide according to (1) [16].

$$R'\mathrm{MgBr} + \mathrm{HgBr_2} \rightarrow R'\mathrm{HgBr} + \mathrm{MgBr_2} \qquad (1)$$

However, all attempts to form the intermediate Grignard reagents were unsuccessful, whether using diethylether or THF as solvent, extended reflux times, different types and grades of magnesium, or using the various stratagems commonly employed to initiate reaction [17, 18].

Organolithium derivatives are purported to react easily with mercury(II) halides [19, 20], the lithiated species again not being isolated but reacting *in situ* with, for example, mercury(II) bromide according to (2).

$$R'\mathrm{Li} + \mathrm{HgBr_2} \rightarrow R'\mathrm{HgBr} + \mathrm{LiBr} \qquad (2)$$

This route to the 4-(4′-*n*-alkoxybiphenyl)mercury(II) bromides **2** was thus explored and eventually led to their successful preparation by the addition of a solution of the appropriate 4-alkoxy-4′-lithiobiphenyl, prepared by room-temperature reaction of 4-alkoxy-4′-bromobiphenyl **1** with *n*-butyllithium in diethylether, to a solution of mercury(II) bromide also in diethylether and at ambient temperature.

Successful formation of the organolithium was confirmed by a control experiment in which a slight excess of *n*-butyllithium was added to a solution of 4-bromo-4′-propoxybiphenyl (**1b**) in diethylether at room temperature. After stirring for 30 min and quenching with one mol equivalent of water, 4-propoxybiphenyl was quantitatively recovered, thus establishing the reactivity of the 4-alkoxy-4′-bromobiphenyls **1** towards bromine–lithium exchange and verifying the integrity of the rest of the molecule after treatment with *n*-butyllithium at room temperature.

The most critical factor in the preparation was the method of reagent addition; slow addition of the solution of the lithio derivative to the mercury(II) bromide solution was required to avoid the formation of metallic mercury always experienced upon inverse addition of these reagents. It appears that in the presence of an excess of the mercury salt the preferred reaction is attack of this species on the organolithium rather than reduction of mercury(II).

We found that the temperature was also important: in experiments performed at −78°C the yield of the organomercury(II) bromide was much reduced. Reactions with *n*-butyllithium and similar organolithium reagents are invariably carried out at low temperature to protect such functional groups as $C{=}O$ and $C{\equiv}N$, which are liable to react with the lithiated species [20]; such functionalities are not present in the biphenyl systems under consideration here. Competitive metallation of *ortho* hydrogens made acidic by the adjacent halogen atom was also not observed.

We also found that the use of mercury(II) chloride in place of the bromide was undesirable as the resultant organomercury(II) chloride, when isolated in the solid state, appeared to be unstable, with portions of the material turning an orange-brown colour on standing for a short time in air. Finally, it is noted that although reactions could be carried out using THF as solvent, best results were achieved using diethylether.

Considerable effort was expended in attempting to obtain pure samples of the organomercury(II) bromides **2a–e**. The crude products were always obtained together with a contaminant which melted between 214 and 223°C and a small amount of a second, much higher-melting compound (m.p. > 380°C). The latter material was possibly the by-product lithium bromide (lit. [21] m.p. 552°C) and the former was shown (see below) to be unreacted mercury(II) bromide (lit. [21] m.p. 236°C), the melting point of which was depressed in the mixture. Unfortunately the crude products were profoundly insoluble in all common organic solvents and mixtures thereof, precluding purification by either chromatography or recrystallization. In DMSO the solid turned black and a degree of dissolution seemed to occur but this proved inadequate for the purposes of NMR spectroscopy. Extraction of the contaminants into hot methanol, in which both mercury(II) bromide and lithium bromide are soluble, was also not successful as filtration was complicated by the extremely fine particle size of the precipitate, resulting in substantial loss of material. Purification by vacuum sublimation was attempted but control of temperature and pressure was not fine enough to effect separation of the required product from mercury(II) bromide, although the sublimed material did appear to be free of the second, higher-melting contaminant, which remained unsublimed as a brown residue in the cold-finger apparatus.

Consequently, no analytical or spectroscopic data for the organomercury (II) bromides **2a**–**e** are presented; indeed, their successful preparation is only proved by the realization of their subsequent reaction with dithizone to give the corresponding organomercury(II) dithizonates in analytical purity.

4-(4′-n-Alkoxybiphenyl)mercury(II) Dithizonates (3a–e)

Finally, the dithizonate complexes **3a**–**e** were prepared by a new procedure in which triethylamine was used to deprotonate the dithizone ligand in a dichloromethane monophase, this method proving to be quicker and more convenient than the classical aqueous ammonia–chloroform extraction system used previously [10, 22]. Due to the presence of small amounts of unreacted mercury(II) bromide in the crude organomercury(II) bromides **2a**–**e**, two reaction products were always formed and these were separated by column chromatography on silica using toluene as the eluent. The first-eluted, less polar compound was shown by ^{1}H NMR spectroscopy to be the required 4-(4′-*n*-alkoxybiphenyl)mercury(II) dithizonate **3**, while the identity of the second product, which might have been either the mercury(II) bis(dithizonate), $Hg(Hdptc)_2$, or the mono-chelate complex HgBr(Hdptc), was established as the former by comparison of its melting point with that of an authentic sample of $Hg(Hdptc)_2$. The yield of this material was always some 20–30% of that of the desired organomercury(II) dithizonate **3**.

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 accomplished 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 [23].

The mass spectra (EI ionization) of **3c**, **d** and **e** were obtained, with only compound **3d** giving a molecular ion. Most of the peaks corresponding to the successive loss of methylene units from the alkoxy chains were detected. A strong peak at *m/z* 422 was observed in the spectrum of **3e**, corresponding to the loss of the dithizonato ligand from the molecular ion, while a peak at *m/z* 508 in this spectrum may represent the recombination of the dithizonato moiety with a phenyl radical. An interesting feature present in the spectra of all three compounds is the existence of relatively strong peaks at *m/z* 167, 168 and 169. These peaks are also observed in the mass spectrum of dithizone and have been attributed to the formation of diphenylamine and its rearrangement to carbazole [24]. For compounds **3d** and **3e** the peak at *m/z* 169 is further reinforced by the fragment $C_{12}H_{25}^+$.

Thermal Behaviour

Because of the rod-like shape of the long hydrocarbon chain and the high anisotropy of polarizability of the biphenyl group, there is potential in these compounds to display the liquid-crystalline properties of a calamitic metallomesogen [25]. Indeed, the combination of the two phenomena of photochromism and liquid crystallinity in a single compound (as opposed to the dissolution of a photochromic material in a liquid-crystalline matrix) is an appealing goal [13]. In the event, none of the dithizonate complexes **3a–e** 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 except for **3a**, which decomposed upon melting. The melting points (as the onset temperatures determined from the DSC thermograms) are reported in the Experimental section and manifest the expected trend of decreasing m.p. with increasing length of the alkoxy chain.

The lack of any mesomorphic behaviour in the organomercury(II) dithizonates **3a–e** can be attributed to the overall shape of the dithizonato ligand, in which the geometry and bulk of the phenyl groups are probably sufficient to overcome any tendency of the long-chain 4-(4′-*n*-alkoxybiphenyl)mercury(II) system to form the parallel arrangement of molecules which exists in and defines the calamitic liquid-crystalline state [25]. Unfortunately, analogues of dithizone with smaller entities, *e.g.*, methyl, replacing the phenyl groups have for many years evaded synthesis [1, 26] and none is currently known.

Photochromic Behaviour

When solutions of the long-chain organomercury(II) dithizonates **3a–e** in organic solvents were irradiated with visible light, a reversible colour change from yellow to blue was observed. This behaviour is similar to the photochromism exhibited by the parent compound, mercury(II) bis(dithizonate) [4–8]. The visible absorption spectra of **3a–e** as chloroform solutions were recorded in the range 400–700 nm. The results are collected in Table I and typical spectra are reproduced in Figure 1, where the single isosbestic point between the absorption maxima of the normal and photoactivated forms indicates the absence of reaction intermediates or side reactions. 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 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.

We found that the visible absorption maxima of both the yellow and blue forms were 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].

While the half-life of the labile blue form of the parent mercury(II) bis(dithizonate) in chloroform is of the order of one minute [7, 8, 27], we found that the same parameter for the organomercury(II) dithizonates **3a–e** was consistently increased. Difficulty was encountered in obtaining reproducible thermal return rates for these compounds, but a qualitative study

TABLE I Visible absorption spectral data for normal yellow and photoactivated blue forms of **3a–e** measured in $CHCl_3$ solution (ca. 10^{-5} mol dm^{-3})

	λ_{max}/nm[a]		
Complex	*Yellow form*	*Blue form*	$t_{1/2}/min$[b]
3a	486 (3950)	598	3
3b	486 (3800)	598	3
3c	486 (4100)	599	5
3d	487 (4250)	599	6
3e	488 (3900)	599	9

[a] The absorption coefficient (ε/m^2 mol^{-1}) is given in parentheses for the yellow form only.

[b] The half-life of the labile blue form ($t_{1/2}$) was estimated from several measurements and is strongly sensitive to traces of water and other contaminants (see text). The error associated with these estimates is ca. 1 min.

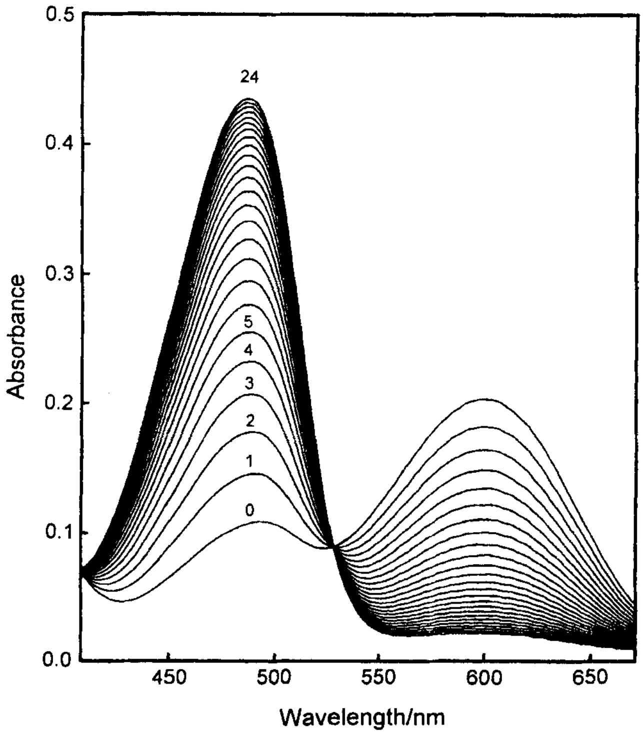


FIGURE 1 Visible absorption spectra of return reaction of **3c** (1.06×10^{-5} mol dm^{-3} in dry $CHCl_3$) after irradiation with visible light. The numbers on selected curves indicate the time in minutes after starting the first scan; spectra were run at 1 min intervals.

indicated that the half-lives increased with increasing chain length of the alkoxy substituent, and a maximum value of $t_{1/2}$ = ca. 9 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, 22] accounts for the poor reproducibility observed for the thermal return rates.

The photochromism does not appear to proceed at a measurable rate in the absence of a solvent. Samples of **3a–e** were separately smeared onto glass slides and irradiated through IR- and UV-absorbing filters: the materials all appeared to decompose on continued exposure, with a degree of darkening being observed after one hour and this increasing with time. Indeed, no orange → violet colour change was observed as was reported for the mercury(II) bis(dithizonate) complex [7] and the experiment was discontinued after 6 hours.

CONCLUSIONS

We have shown that a new series of organomercury(II) dithizonate complexes containing long-chain alkoxybiphenyl groups can be synthesized if meticulous attention is paid to the reaction conditions. A useful new procedure was developed for the final dithizone complexation step. The resulting materials are not mesomorphic but do display a reversible yellow ⇌ blue photochromism when chloroform solutions are irradiated with visible light, and the half-lives of the metastable blue forms are substantially increased relative to that of the parent mercury(II) bis(dithizonate) complex.

EXPERIMENTAL

General

^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were obtained at 400 and 100 MHz, respectively, on a Varian Unity-400 instrument. Chemical shifts are quoted relative to tetramethylsilane and the coupling constants, *J*, are given in hertz. Mass spectra (EI ionization) were recorded on a modified Kratos MS 80RF spectrometer. 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, the single figures quoted for the melting points are the onset temperatures as determined from the DSC thermograms, which were recorded on a Perkin Elmer DSC-7 instrument at heating and cooling rates of 10°C min^{-1} and with a nitrogen flow-rate of 40 $cm^3 min^{-1}$. The instrument was calibrated with indium (156.6°C, 28.45 $J g^{-1}$) and zinc (419.47°C, 108.37 $J g^{-1}$).

Visible absorption spectra were recorded on a Philips PU-8720 scanning 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 visible radiation 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. $10^{-5} mol\,dm^{-3}$) 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 trying 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

All reagents used in the preparative work were analytically pure and mostly supplied by Aldrich. Solvents were purified according to standard procedures. Diethylether was pre-dried over sodium wire. All glassware was oven-dried and, in the case of reactions involving *n*-butyllithium, flamed before use; the reaction flasks were flushed with dry nitrogen gas before and during reagent addition and a nitrogen atmosphere was maintained during all reactions.

4-(4′-n-Alkoxybiphenyl)mercury(II) Bromides (2a – e)

In a typical procedure, described here in detail for the preparation of the 4-(4′-tetradecyloxybiphenyl)mercury(II) bromide **2d**, a 1.6-M solution of *n*-butyllithium in hexane (0.67 cm^3, 1.08 mmol) was added to a solution of 4-tetradecyloxy-4′-bromobiphenyl **1d** (0.40 g, 0.90 mmol) in diethylether (5 cm^3) at room temperature. A slightly murky solution was obtained and this was stirred at room temperature for 30 min. The solution was then slowly transferred under a positive pressure of nitrogen *via* a metal cannula to a solution of mercury(II) bromide (0.32 g, 0.90 mmol) in diethylether (5 cm^3) at room temperature. A fluffy white precipitate formed immediately and the resulting mixture was left to stir at room temperature for 1 h. The volume of the solvent was then reduced to approximately half by evaporation in a stream of nitrogen gas and the solid was isolated by filtration through a fine grade of filter paper. After drying overnight *in vacuo* over silica gel, 0.55 g of the impure intermediate product **2d** was obtained, which was carried straight through to the next stage. Wide-ranging attempts to obtain pure samples of **2a – e** were to no avail (see Discussion section).

4-(4′-n-Alkoxybiphenyl)mercury(II) Dithizonates (3a – e)

Again, we describe in detail the procedure followed to obtain the 4-(4′-tetradecyloxybiphenyl)mercury(II) dithizonate **3d** as being representative of the general method. The crude 4-(4′-tetradecyloxybiphenyl)mercury(II) bromide **2d** (0.55 g) was suspended in dichloromethane (50 cm^3), to which solid dithizone (analytical grade, 0.22 g, 0.86 mmol; calculated by assuming a 100% yield of the intermediate **2d**) was added in a single portion; a red, turbid mixture was immediately obtained. Addition of a few drops of triethylamine gave a clear, red solution; this was allowed to stir for 15 min and a small quantity of undissolved black material was then filtered off. The filtrate was concentrated to dryness under reduced pressure and the residue was chromatographed on a silica gel column using toluene as the eluent to give the desired organomercury(II) dithizonate **3d** (0.32 g, 43% based on **1d**) and mercury(II) bis(dithizonate) (85 mg) as a by-product resulting from the presence of unreacted $HgBr_2$ in the crude intermediate **2d**.

Compounds **3a–e** gave the following experimental data (^{1}H and ^{13}C NMR assignments for the aromatic hydrogen and carbon atoms are referenced to the arbitrary numbering scheme depicted in Figure 2; the ^{13}C assignments should be considered to be tentative in the case of the aromatic carbon atoms):

4-(4′-Butoxybiphenyl)mercury(II) Dithizonate (3a) 0.33 g, 49%; m.p. 178°C (dec.) (Found: C, 50.9; H, 4.0; N, 8.1. $C_{29}H_{28}HgN_4OS$ requires C, 51.1; H, 4.1; N, 8.2%); δ_H 1.00 (3H, *t*, CH_3), 1.53 (2H, sextet, CH_3CH_2), 1.81 (2H, quintet, OCH_2CH_2), 4.02 (2H, *t*, OCH_2), 6.99 (2H, *d*, $J_{2,3}$ 8.4, H^2), 7.08 (1H, *m*, H^{16}), 7.40 (7H, *m*, H^{11}, H^{12}, H^{14} and H^{15}), 7.48 (2H, *d*, $J_{6,7}$ 7.6, H^6), 7.55 (2H, *d*, $J_{3,2}$ 8.0, H^3), 7.61 (2H, *d*, $J_{7,6}$ 7.2, H^7), 7.95 (2H, *m*, H^{10}) and 9.21 (1H, br s, NH).

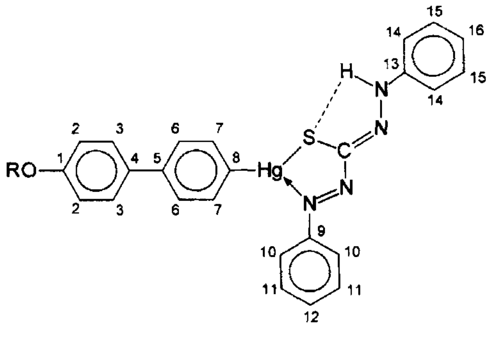


FIGURE 2 Numbering system for NMR assignments of aromatic hydrogen and carbon atoms in **3a–e** and mercury(II) bis(dithizonate) (where a second dithizonato group replaces the indicated alkoxybiphenyl group).

*4-(4′-Pentyloxybiphenyl)mercury(II) Dithizonate (**3b**)* 0.21 g, 32%; m.p. 171°C (Found: C, 51.5; H, 4.2; N, 7.95. $C_{30}H_{30}HgN_4OS$ requires C, 51.8; H, 4.35; N, 8.1%); δ_H 0.95 (3H, *t*, CH_3), 1.44 [4H, *m*, $CH_3(CH_2)_2$], 1.82 (2H, quintet, OCH_2CH_2), 4.01 (2H, *t*, OCH_2), 6.99 (2H, *d*, $J_{2,3}$ 8.8, H^2), 7.08 (1H, *m*, H^{16}), 7.40 (7H, *m*, H^{11}, H^{12}, H^{14} and H^{15}), 7.49 (2H, *d*, $J_{6,7}$ 8.4, H^6), 7.55 (2H, *d*, $J_{3,2}$ 9.0, H^3), 7.62 (2H, *d*, $J_{7,6}$ 8.0, H^7), 7.96 (2H, *m*, H^{10}) and 9.21 (1H, br s, NH).

*4-(4′-Decyloxybiphenyl)mercury(II) Dithizonate (**3c**)* 0.19 g, 32%; m.p. 166°C (Found: C, 54.8; H, 5.2; N, 7.2. $C_{35}H_{40}HgN_4OS$ requires C, 54.9; H, 5.3; N, 7.3%); δ_H 0.89 (3H, *t*, CH_3), 1.29 [12H, *m*, $(CH_2)_6$], 1.48 (2H, *m*, $OCH_2CH_2CH_2$), 1.80 (2H, quintet, OCH_2CH_2), 4.01 (2H, *t*, OCH_2), 6.99 (2H, *d*, $J_{2,3}$ 8.8, H^2), 7.08 (1H, *m*, H^{16}), 7.40 (7H, *m*, H^{11}, H^{12}, H^{14} and H^{15}), 7.49 (2H, *d*, $J_{6,7}$ 8.4, H^6), 7.55 (2H, *d*, $J_{3,2}$ 8.8, H^3), 7.62 (2H, *d*, $J_{7,6}$ 8.4, H^7), 7.95 (2H, *m*, H^{10}) and 9.21 (1H, br s, NH); δ_C 14.13 (CH_3), 22.69 (CH_3CH_2), 26.08 ($CH_3CH_2CH_2$), 29.32–29.59 [$(CH_2)_5$], 31.91 (OCH_2CH_2), 68.15 (OCH_2), 114.88 (C^2), 115.18 (C^{14} or C^{15}), 123.05 (C^{10} or C^{16}), 123.33 (C^{16} or C^{10}), 127.10 (C^6 or C^7), 128.07 (C^7 or C^6), 129.44 (C^{11} or C^{14} or C^{15}), 130.75 (C^{12}), 137.12 (C^8), 140.93 (C^3), 142.15 (C^9 or C^{13}), 150.43 (C^{13} or C^9), 152.89 (CS) and 158.95 (C^1); *m*/*z* 170, 169, 168, 167, 155, 141, 85, 71, 57 and 43.

*4-(4′-Tetradecyloxybiphenyl)mercury(II) Dithizonate (**3d**)* 0.32 g, 43%; m.p. 155°C (Found: C, 56.85; H, 5.7; N, 6.7. $C_{39}H_{48}HgN_4OS$ requires C, 57.0; H, 5.9; N, 6.8%); δ_H 0.88 (3H, *t*, CH_3), 1.27 [22H, *m*, $(CH_2)_{11}$], 1.81 (2H, quintet, OCH_2CH_2), 4.01 (2H, *t*, OCH_2), 6.99 (2H, *d*, $J_{2,3}$ 9.2, H^2), 7.08 (1H, *m*, H^{16}), 7.41 (7H, *m*, H^{11}, H^{12}, H^{14} and H^{15}), 7.49 (2H, *d*, $J_{6,7}$ 8.0, H^6), 7.55 (2H, *d*, $J_{3,2}$ 8.8, H^3), 7.62 (2H, *d*, $J_{7,6}$ 8.0, H^7), 7.96 (2H, *m*, H^{10}) and 9.23 (1H, br s, NH); δ_C 14.13 (CH_3), 22.70 (CH_3CH_2), 29.07 ($CH_3CH_2CH_2$), 29.31–29.68 [$(CH_2)_9$], 31.93 (OCH_2CH_2), 68.15 (OCH_2), 114.88 (C^2), 115.18 (C^{14} or C^{15}), 123.05 (C^{10} or C^{16}), 123.33 (C^{16} or C^{10}), 127.10 (C^6 or C^7), 128.07 (C^7 or C^6), 129.34 (C^{11} or C^{14} or C^{15}), 129.45 (C^{11} or C^{14} or C^{15}), 130.75 (C^{12}), 132.88 (C^4 or C^5), 137.13 (C^8), 140.93 (C^3), 142.15 (C^9 or C^{13}), 150.43 (C^{13} or C^9), 152.49 (CS) and 158.96 (C^1); *m*/*z* 837 (M^+), 169, 168, 167, 155, 141, 113, 99, 85, 71, 57 and 43.

*4-(4′-Octadecyloxybiphenyl)mercury(II) Dithizonate (**3e**)* 0.15 g, 28%; m.p. 114°C (Found: C, 58.6; H, 6.2; N, 6.25. $C_{43}H_{56}HgN_4OS$ requires C, 58.85; H, 6.4; N, 6.4%); δ_H 0.88 (3H, *t*, CH_3), 1.26 [30H, *m*, $(CH_2)_{15}$], 1.80 (2H, quintet, OCH_2CH_2), 4.01 (2H, *t*, OCH_2), 6.99 (2H, *d*, $J_{2,3}$ 9.2, H^2), 7.08 (1H, *m*, H^{16}), 7.41 (7H, *m*, H^{11}, H^{12}, H^{14} and H^{15}), 7.49 (2H, *d*, $J_{6,7}$ 8.0, H^6), 7.54 (2H, *d*, $J_{3,2}$ 8.8, H^3), 7.62 (2H, *d*, $J_{7,6}$ 8.0, H^7), 7.96 (2H, *m*, H^{10}) and 9.22 (1H, br s, NH); *m/z* 508, 422, 169, 168, 167, 155, 141, 85, 71, 57 and 43.

The bis-dithizonate by-product, $Hg(Hdptc)_2$, gave the following experimental data: m.p. 220–223°C (lit. [10] 223–224°C) (Found: C, 43.55; H, 3.0; N, 15.7. Calc. for $C_{26}H_{22}HgN_8S_2$: C, 43.9; H, 3.1; N, 15.8%); δ_H 7.10 (2H, *m*, H^{16}), 7.31 (6H, *m*, H^{12} and H^{14} or H^{15}), 7.42 (8H, *m*, H^{11} and H^{15} or H^{14}), 7.74 (4H, *m*, H^{10}) and 9.33 (2H, br s, NH); δ_C 115.09 (C^{14} or C^{15}), 122.85 (C^{10}), 123.74 (C^{16}), 129.39 (C^{11} or C^{14} or C^{15}), 129.54 (C^{11} or C^{14} or C^{15}), 130.90 (C^{12}), 142.07 (C^9 or C^{13}), 150.43 (C^{13} or C^9) and 152.89 (CS); *m/z* 711 (M^+), 618, 255, 226, 169, 168, 167, 105, 93 and 77.

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