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# The Photochemical Properties of the Mono- and Dithioimide Derivatives of (*E*,*E*)-Dibenzylidene-N-Phenylsuccinimide

P. Adriaan Davidse and Jan L. M. Dillen*

*Department of Chemistry, University of Pretoria, Pretoria, 0002, South Africa*

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## ABSTRACT

*Novel (E,E)-dibenzylidene-N-phenyl succinimide thioimide* **1b** *and dithioimide* **1c** *derivatives of the photochromic fulgimide* **1a** *were synthesized. The thioimide* **1b** *and dithioimide* **1c** *derivatives were found to undergo isomerization as the main photoreaction when irradiated in a variety of organic solvents, as opposed to the reversible electrocyclic ring closure/opening reactions in the case of the fulgimide* **1a**. *The X-ray crystal structures of* **1b** *and* **1c** *were determined, and the influence of the thiocarbonyl groups on the structural parameters were investigated in comparison to the crystal structure of* **1a**. *The $^1H$ and $^{13}C$ NMR spectra were recorded for all three compounds* **1a**, **1b**, *and* **1c** *and are discussed in terms of their structural and electronic variations, as is the effect on the photochemical behavior. The twisting of the N-phenyl ring was found to be a consequence of intramolecular steric interactions and not of intermolecular packing forces. This was substantiated by a series of semiempirical (AM1) calculations. The C(thiocarbonyl) was found to be highly deshielded compared to the corresponding C(carbonyl) carbon atom, and the deshielding effect of the thiocarbonyl group was evident throughout the whole thiocinnamic moiety. Crystal data for monothioimide* **1b**: *spacegroup $P2_1/c$ with $a = 8.794(2)$ Å, $b = 9.623(1)$ Å, $c = 22.182(5)$ Å, $\beta = 91.45(2)°$, $Rw = 0.038$, and $R = 0.067$. Dithioimide* **1c**: *spacegroup Pnna with $a = 9.411(2)$ Å, $b = 17.304(2)$ Å, $c = 13.574(2)$ Å, $Rw = 0.055$, and $R = 0.077$.*

## *INTRODUCTION*

The photochromic behavior of fulgide-fulgimide type compounds has been studied since early on [1], and, recently, we have also reported studies on the first photochromic thiofulgide derivative [2]. Substitution of the $sp^3$ oxygen atom in the anhydride structure of fulgides with sulfur to form the thioanhydride derivative has been shown to have a significant effect on the charge distribution in the $4n + 2$ $\pi$-system that is involved in the electrocyclic ring closure reaction and consequently has a marked influence on the photochromic behavior of these thiofulgide derivatives.

Substitution of the carbonyl groups by thiocarbonyl groups was expected to have an even greater effect on the photochemical behavior, as the nature of the two independent chromophores may be significantly influenced. Due to the lower stability of thiocarbonyl compounds compared to their corresponding carbonyl derivatives, such compounds are fairly uncommon. Stable thiocarbonyl compounds are obtained if substituents, like nitrogen, are present in the $\alpha$-position, which stabilize the thiocarbonyl group by decreasing the C=S double bond character.

2,4-Bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide A, commonly known as Lawessons reagent, was exclusively used as a source of sulfur in the thiating reactions, as it was found to give reproducible results—usually in high

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Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

*To whom correspondence should be addressed.

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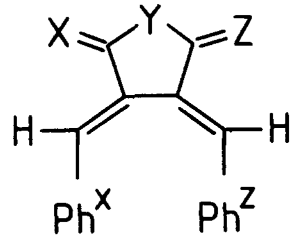

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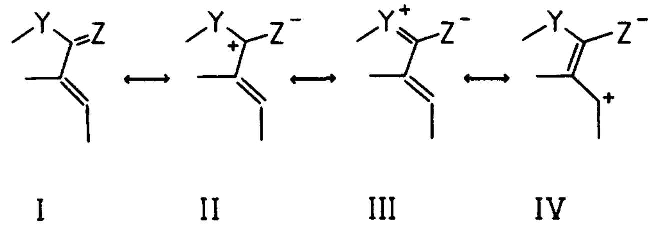

SCHEME 2

yields—even with molecules containing other functional groups.

Stable thioderivatives of imides have previously been synthesized [3,4] with $P_4S_{10}$, and their chemistry has been investigated. In the case of N-substituted compounds, only low yields have been obtained. Mono- and dithioimides have more recently been prepared [5] in much higher yield with the more convenient thiation reagent A. Similarly, when the imide **1a** reacted with A (mole ratio 2:1) in refluxing benzene, a moderate yield of the monothioimide **1b** was obtained with some dithioimide **1c** also present. When the mole ratio was changed to 1:1, the dithioimide was formed in higher yield and much less of the monothioimide could be isolated. Both these products are stable compounds and both have been shown to be the *E,E*-isomers by X-ray diffraction analysis.

However, the enhanced photosensitivity of the thioanhydride [2] was not paralleled in either the mono- or dithioimide derivatives, which did not undergo photochemically induced ring closure but have been found to undergo $E \rightleftharpoons Z$ isomerization as the main photochemical reaction, even after irradiation of 40 hours with UV light. This could mainly be a consequence of the lowering of the barrier of rotation [6,7] around the $\alpha,\beta$-ethylenic double bond by greater delocalization over the thiocarbonyl group, giving rise to an excited state, which can be represented as a dipolar structure IV leading mainly to $E \rightleftharpoons Z$ isomerization. The observation [8] that a thiocarbonyl group is more strongly electron withdrawing by resonance and more weakly so by induction than a carbonyl group has also been investigated in the title compounds by nuclear magnetic resonance (NMR) spectroscopy. The influence of the above-mentioned feature of the thiocarbonyl group on the photochemical behavior of **1b** and **1c** was also investigated. Both $\beta$-H and *o*-$Ph^Y$ protons were markedly effected by the electronic structure in the series **1a** → **1b** → **1c**, which also significantly influenced the $^{13}C$ NMR spectra.

TABLE 1 Compound Numbering and Geometrical Structures of Heteroatomic Derivatives of **1d**

| *Compound* | *X* | *Y* | *Z* |
|---|---|---|---|
| **1a** | O | $NPh^Y$ | O |
| **1b** | S | $NPh^Y$ | O |
| **1c** | S | $NPh^Y$ | S |
| **1d** | O | O | O |
| **1e** | O | S | O |

Comparison of the crystal structures of **1b** and **1c** with that of the known structure of **1a** [9] shows the differences in the bond lengths arising from the introduction of the thiocarbonyl group. When compared to the calculated (by AM1) values, the increase in the dihedral angle between the N-phenyl group and the five-membered succinimide ring in the series **1a** → **1b** → **1c** seemed to be a consequence of the increased intramolecular steric interactions between the larger thiocarbonyl group and the N-phenyl ring than due to intermolecular packing forces.

## *RESULTS AND DISCUSSION*

The increase in conjugation in the chromophore due to the better resonance stabilization of the thiocarbonyl groups, which mainly gives rise to the reversible $E \rightleftharpoons Z$ isomerization as the major photoreaction [10], is clearly evident by the marked bathochromic shifts of 38.0 nm and 64.4 nm in the thioimide derivatives **1b** and **1c**, respectively, compared to the imide **1a** (Figure 1).

The crystal structures of **1b** and **1c** were determined by X-ray crystallography and compared to the known structure of **1a** [9]. Selected molecular parameters, relevant to the discussion of the structural relationship of compounds **1a**, **1b**, and **1c**, are listed in Table 2. Figures 2 and 3 show the atomic numbering and perspective drawings of **1b** and **1c**, respectively. The crystallographically imposed twofold rotational symmetry around the N(1)–C(22) bond with atoms C(25), C(22), and N(1) lying on the rotational axes for the dithioimide **1c** is similar to the imide **1a** [9].

To our knowledge, no X-ray structures of any cyclic five-membered monothioimide or dithioimide systems have been determined to date. The crystal structures of the novel compounds **1b** and **1c** reported here are therefore not only of interest

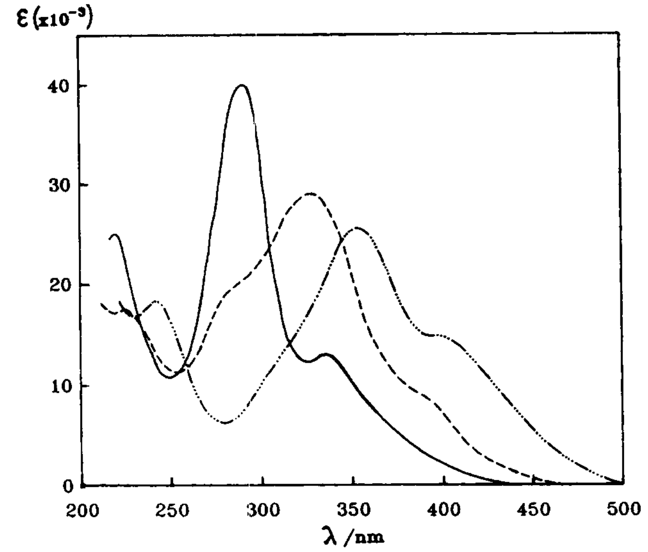

**FIGURE 1** The UV absorption spectra of **1a** (—), **1b** (---), and **1c** (-···) in dichloromethane at room temperature.

**TABLE 2** Selected Bond Lengths (Å) and Bond Angles (°) of Compounds **1a, 1b, 1c** Obtained by X-Ray Diffraction (Standard Deviations in Parentheses)

| | **1a** | **1b** | **1c** |
|---|---|---|---|
| Y(1)–C(2) | 1.392(2) | 1.386(5) | 1.388(4) |
| Y(1)–C(5) | 1.392(2) | 1.414(5) | 1.388(4) |
| C(2)=X(7) | 1.203(2) | 1.620(4) | 1.639(4) |
| C(5)=Z(6) | 1.203(2) | 1.234(5) | 1.639(4) |
| C(2)–C(3) | 1.496(2) | 1.491(5) | 1.489(5) |
| C(3)–C(4) | 1.452(2) | 1.463(5) | 1.479(7) |
| C(4)–C(5) | 1.496(2) | 1.504(5) | 1.489(5) |
| C(3)=C(8) | 1.349(2) | 1.335(5) | 1.349(5) |
| C(4)=C(15) | 1.349(2) | 1.342(6) | 1.349(5) |
| C(8)–C(9) | 1.460(2) | 1.464(6) | 1.458(5) |
| C(15)–C(16) | 1.460(2) | 1.454(6) | 1.458(5) |
| Y(1)–C(22) | 1.432(3) | 1.440(5) | 1.444(6) |
| C(2)–Y(1)–C(5) | 112.2(1) | 113.3(4) | 112.6(2) |
| Y(1)–C(2)–C(3) | 106.7(1) | 106.4(4) | 106.9(4) |
| C(2)–C(3)–C(4) | 106.1(1) | 106.3(4) | 105.4(2) |
| C(3)–C(4)–C(5) | 106.1(1) | 106.5(4) | 105.4(2) |
| Y(1)–C(5)–C(4) | 106.7(1) | 105.2(4) | 106.9(4) |
| Y(1)–C(2)=X(7) | 125.1(1) | 125.0(3) | 124.2(3) |
| Y(1)–C(2)=Z(6) | 125.1(1) | 126.1(4) | 124.2(3) |
| X(7)=C(2)–C(3) | 128.2(1) | 128.6(3) | 128.9(3) |
| Z(6)=C(5)–C(4) | 128.2(1) | 128.6(4) | 128.9(2) |
| C(2)–C(3)=C(8) | 117.0(1) | 119.5(4) | 118.2(4) |
| C(5)–C(4)=C(15) | 117.1(1) | 117.0(4) | 118.2(4) |
| C(8)=C(3)–C(4) | 136.1(1) | 133.5(4) | 135.5(3) |
| C(15)=C(4)–C(3) | 136.1(1) | 136.0(4) | 135.5(3) |
| C(3)=C(8)–C(9) | 129.7(1) | 130.6(4) | 132.1(3) |
| C(4)=C(15)–C(16) | 129.7(1) | 131.4(4) | 132.1(3) |
| C(2)–Y(1)–C(22) | 123.9(1) | 125.1(4) | 123.7(2) |
| C(5)–Y(1)–C(22) | 123.9(1) | 121.5(4) | 123.7(2) |

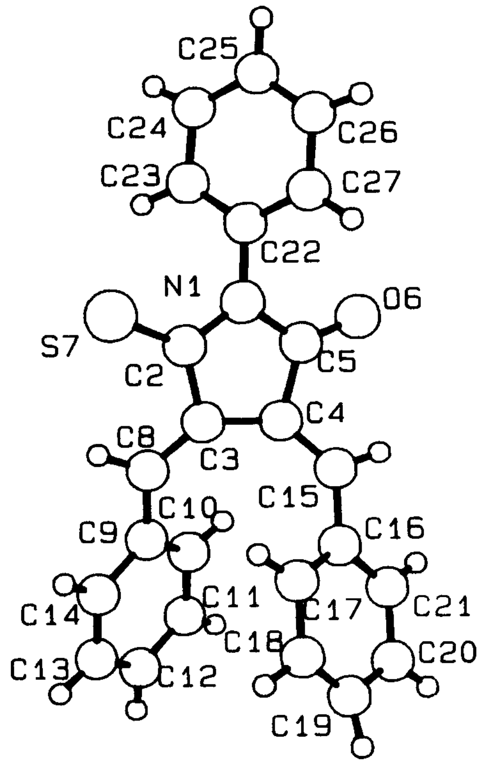

**FIGURE 2** A perspective view of the molecule **1b** with atomic numbering.

in relation to their photochromic behavior but are also important for the understanding of the fundamental structural features of such systems.

As the bond angles for all three compounds are similar, and the bond lengths vary on going from **1a** to **1b** to **1c**, it would seem that the electronic influence of the introduction of the thiocarbonyl group on the cinnamic system is much more important than the steric influence of the larger sulfur atom.

The concept that the thiocarbonyl group of thioimides has stronger resonance interaction with the adjacent nitrogen atom than the carbonyl group of imides is supported by the fact that the N(1)–C(2) bond (1.386(5) Å) in **1b** is shorter than the N(1)–C(5) bond (1.414(5) Å). As a consequence of the stronger electron-withdrawing effect (by resonance) of the thiocarbonyl group and consequent weaker conjugative interaction of the carbonyl group with the nitrogen, the C(5)=O(6) bond in **1b** (1.234(5) Å) is longer than the corresponding bond in the symmetrical imide **1a** (1.203(2) Å). Also, the slightly longer C(2)=S(7) bond (1.637(4) Å) in **1b** relative to **1c** could be explained if, in the symmetrical dithioimide **1c**, the electron density on the nitrogen is "shared" equally by two thiocarbonyl groups on either side of this atom.

The N(1)–C(22) bond length in **1a** (1.432 Å) is comparable to the mean length (1.429 Å) of the

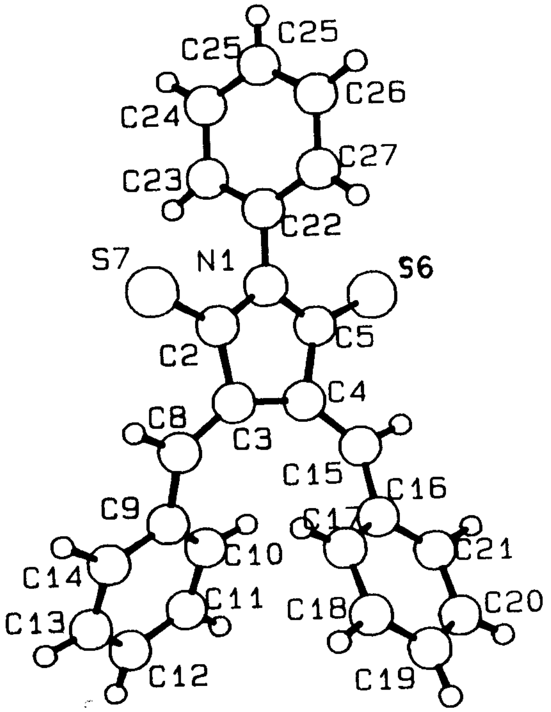

FIGURE 3 A perspective view of the molecule **1c** with atomic numbering.

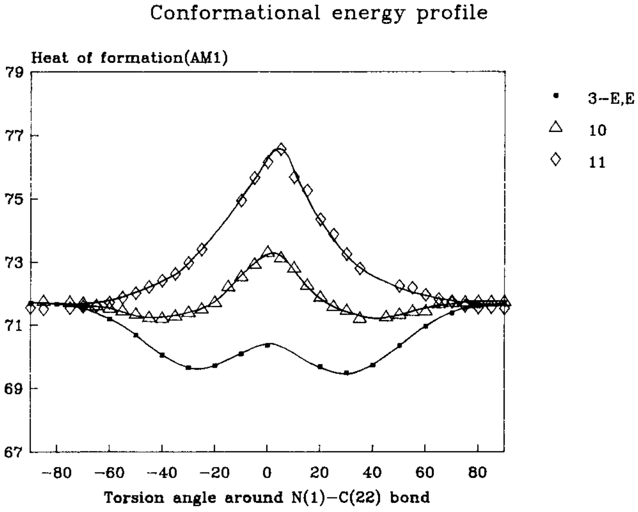

FIGURE 4 Comparison of relative heats of formation between the compounds **1a**, **1b**, and **1c**.

N(1)–C(22) bond in the earlier mentioned, related succinimides [11]. This is shorter than a normal C–N bond and longer than a normal C=N bond. From comparison of this bond length with those of a conjugated N–C($\alpha$) bond (1.45 Å) in peptide linkages [12], the C–N bond (1.412–1.483 Å) in aniline derivatives [13,14] and the two C–N bonds (1.378–1.433 Å) in 1,3-diphenylspiro-[imidazolidine-2,2-indane]-1′,3′-dione [15], Taira *et al.* [11] concluded that this C–N bond shows partial double-bond character, which suggests that the N(1)–C(22) bond participates in the conjugated system of the benzene ring. The longer N(1)–C(22) bond lengths in **1b** and **1c** (1.440(5) Å and 1.444(6) Å, respectively) may be due to the lower electron density on the nitrogen of the thioimide in comparison with the imide, as a consequence of the increased resonance interaction with the thiocarbonyl groups.

Due to the stronger electron-withdrawing power (by resonance) of the thiocarbonyl group, the increased conjugation over the cinnamic system is expected to reduce the conjugation over the 1,4-diphenyl-1,3-butadiene system. This may be even more so in going from **1a** to **1b** to **1c**, as indicated by the corresponding lengthening of the C(3)–C(4) bond (1.452(3) in **1a**, 1.463(5) Å in **1b**, and 1.479(7) Å in **1c**). As the C(8)=C(3)–C(4)=C(15) torsion angle, which has a marked effect on the conjugation in the 1,3-butadiene system, is similar in all three compounds (37.9(3)°, 33.8(7)°, −39.9(6)° in **1a**, **1b**, and **1c**, respectively), the previous assumption that the change in the conjugation over the 1,3-butadiene system is mainly effected by the electronic influence of the substitution of the carbonyl- with the thiocarbonyl group is substantiated. The only significant difference in the torsion angles of this part of the molecules is the degree of twisting of the phenyl groups. The smaller degree of rotation in the dithioimide **1c** (av 22.6 in **1a**, 27.4 in **1b**, and 12.6 in **1c**) enlarges the conjugation over the cinnamic system even more, which explains why $E \rightleftharpoons Z$ isomerization occurs as the exclusive photoreaction.

In the thioimides **1b** and **1c**, the dihedral angle between the N-phenyl ring [C(22)–C(27)] and the plane of the five-membered succinimide ring [N(1)–C(2)–C(3)–C(4)–C(5)] is −53.2° and −71.7°, respectively. The increase of this angle in the series **1a** → **1b** → **1c** could be related to the increased steric interaction experienced by the N-phenyl ring on introduction of the larger thiocarbonyl group. As just described, the major difference among these three compounds, apart from the variations in the bond distances, is the dihedral angle between the planes of the N-phenyl- and the succinimide or thioimide rings. These values were determined for the crystal state, but it was important to know the relation between the structure in the crystalline state and the stable molecular conformation determined by molecular orbital calculations. We have therefore calculated the dependence of the heats of formation ($\Delta H_f$) of the three compounds (**1a**, **1b**, and **1c**) on the torsion angle $\omega$ C(2)–N(1)–C(22)–C(23) by the AM1 method [16]; changes of $\Delta H_f$ with increments of 5° for $\omega$ were calculated. As shown in Figure 4, the energy profiles of all three compounds are different.

In all three cases, the torsion angle found in the crystal state, $\omega_{obs}$, was at or near the $\omega$ value for the minimum energy, indicating that the observed torsion angle corresponds to the most stable conformation determined by molecular orbital calculations. The reduction of the dihedral angle in **1a** relative to other succinimides therefore does not seem to be a consequence of crystal-packing forces. The sharp increase of the relative energy profile at a torsion angle of 0° in going from **1a** to **1b** to **1c** illustrates the increase in steric interactions experienced by the N-phenyl group in the thioimides.

## *$^1$H NMR SPECTRA*

The chemical shift values for all hydrogen atoms in compounds **1a**, **1b**, and **1c** are given in Table 3. Unambiguous assignments were made with the help of the two-dimensional (2-D) COSY technique. In compounds **1b** and **1c**, a marked downfield shift is observed for the $\beta$-hydrogens of the thiocinnamic moieties relative to the $\beta$-hydrogens of the cinnamic moieties in **1a** and **1b**. Similarly, a downfield shift (although much smaller) is also observed for the *ortho* protons in the thiocinnamic moieties relative to the *ortho* protons in **1a**. These downfield shifts of the resonances of the protons adjacent to the thiocarbonyl group in comparison with a normal carbonyl group may originate either due to an increased diamagnetic deshielding anisotropy or an increase in deshielding caused by a greater mesomeric effect of the C=S group relative to the C=O group. The latter is believed to be more important, since the stronger electron withdrawing character (by resonance) of the sulfur would reduce the double-bond character of the C=S group, thus reducing the deshielding caused by the diamagnetic anisotropy of the C=S double bond. At the same time, the deshielding caused by the mesomeric effect of the C=S group is enlarged relative to the C=O group. Further proof for this is provided by the $^{13}$C NMR spectra of these compounds.

In the series **1a** → **1b** → **1c**, the chemical shifts of the *ortho* protons cannot be related to the rotation of the phenyl rings around the C(8)–C(9) and C(15)–C(16) bonds as the changes in the environment of these protons, due to steric changes (rotation), are overshadowed by the mesomeric effects. Apart from the differences in the *ortho* resonances, no other significant differences in the proton shifts of the *E,E*-phenyl rings are observed. The relative orientation of these phenyl rings is therefore similar to that in **1a**, as is also substantiated by X-ray crystallography.

**TABLE 3** $\delta$ $^1$H Values of the Compounds **1a**, **1b**, and **1c**

| | | **1a** | **1b** | **1c** |
|---|---|---|---|---|
| | $\beta$-H$^X$ | 7.88 | 8.30 | 8.10 |
| | $\beta$-H$^Z$ | 7.88 | 7.78 | 8.10 |
| Ph$^Y$ | *o*-H$^Y$ | 7.50 | 7.41 | 7.32 |
| | *m*-H$^Y$ | 7.51 | 7.56 | 7.58 |
| | *p*-H$^Y$ | 7.41 | 7.48 | 7.51 |
| Ph$^X$ | *o*-H$^X$ | 6.92 | 7.02 | 7.05 |
| | *m*-H$^X$ | 6.83 | 6.84 | 6.86 |
| | *p*-H$^X$ | 7.07 | 7.06 | 7.06 |
| Ph$^Z$ | *o*-H$^Z$ | 6.92 | 6.99 | 7.05 |
| | *m*-H$^Z$ | 6.83 | 6.85 | 6.86 |
| | *p*-H$^Z$ | 7.07 | 7.08 | 7.06 |

The progressively larger degree of rotation of the N-phenyl rings in going from **1a** to **1b** to **1c** (as seen from X-ray analysis) is expected to be largely responsible for the upfield shift of the N-phenyl *ortho* protons due to the diminishing of the deshielding anisotropic effect. It is also evident from the $^1$H NMR spectra that the phenyl rings in all compounds oscillate synchronously through a vertical position at room temperature, the molecules then having a time-average mirror plane symmetry, exactly as previously determined for **1d**. The substituent effect on the barriers of rotation of the phenyl rings could therefore in the future be calculated from low temperature $^1$H NMR studies.

## *$^{13}$C NMR SPECTRA*

Chemical shift data for the individual carbon atoms in compounds **1a**, **1b**, and **1c** are given in Table 4. Unambiguous assignments for $^{13}$C resonances were based on 2-D techniques (HETCORR) for protonated carbons and the SPI technique [17] for quaternary carbons.

The $^{13}$C chemical shifts are invaluable in the

**TABLE 4** $\delta$ $^{13}$C Values of Compounds **1a**, **1b**, and **1c**

| | | **1a** | **1b** | **1c** |
|---|---|---|---|---|
| | C(=X) | 169.31 | 201.20 | 201.77 |
| | C(=Z) | 169.31 | 170.77 | 201.77 |
| | $\alpha$-C$^X$ | 122.43 | 130.04 | 131.38 |
| | $\alpha$-C$^Z$ | 122.43 | 121.62 | 131.38 |
| | $\beta$-C$^X$ | 135.61 | 139.35 | 139.49 |
| | $\beta$-C$^Z$ | 135.61 | 135.96 | 139.49 |
| Ph$^Y$ | *i*-C$^Y$ | 132.13 | 134.92 | 138.52 |
| | *o*-C$^Y$ | 126.47 | 127.97 | 128.42 |
| | *m*-C$^Y$ | 128.99 | 129.18 | 129.37 |
| | *p*-C$^Y$ | 128.27 | 129.13 | 129.37 |
| Ph$^Z$ | *i*-C$^X$ | 134.67 | 134.97 | 135.02 |
| | *o*-C$^X$ | 129.79 | 130.02 | 130.38 |
| | *m*-C$^X$ | 127.06 | 127.13 | 127.33 |
| | *p*-C$^X$ | 129.64 | 129.73 | 129.91 |
| Ph$^Z$ | *i*-C$^Z$ | 134.67 | 134.54 | 135.02 |
| | *o*-C$^Z$ | 129.79 | 130.09 | 130.38 |
| | *m*-C$^Z$ | 127.06 | 127.21 | 127.33 |
| | *p*-C$^Z$ | 129.64 | 129.83 | 129.91 |

evaluation of the electronic structure of molecules. The relative importance and contribution of different resonance structures can therefore be established to demonstrate the influence of the substitution of the different heteroatoms on the molecule as a whole.

The heavy atom effect by which double-bonded heteroatoms produce a downfield shift with increasing atomic number (i.e., decreasing electronegativity) was clearly demonstrated by comparison of the C=O and C=S chemical shifts in the above three compounds (see Table 4). Theoretical studies [18] have suggested a linear relationship between chemical shifts of the carbon nuclei in carbonyl and thiocarbonyl groups. Early measurements [19] indicated that a variety of these compounds conformed to this linear relationship, and in 45 pairs of compounds, a correlation coefficient of 0.9959 was found for Equation 1 [20].

$$\delta(C{=}S) = 1.50 \times \delta(C{=}O) - 57.5 \qquad (1)$$

Several other thiocarbonyl compounds have also been studied [21], but only recently have the correlations on thio compounds containing nitrogen been reported [19]. Interestingly, (C=S) of the compounds **1b** and **1c** can be roughly calculated from (C=O) of compounds **1a** and **1b** by using the previously established Equation 2 [17].

$$\delta(C{=}S) = 1.45 \times \delta(C{=}O) - 46.5 \qquad (2)$$

This was also used as an aid to the assignment. As for the thioanhydride **1e** and the imide **1a** [2], the usual interpretation of the upfield shift of C(=X) of the thioimides **1b** and **1c** from those expected of analogous thioketones (Y = CH2) is made in terms of the contribution from both the mesomeric forms III and IV (see Scheme 2), of which form III is not important in thioketones and which neutralizes positive charge on the thiocarbonyl carbon. Interestingly, the cinnamic and thiocinnamic systems in **1b** and therefore presumably also in **1a** and **1c** seem to form two almost independent $\pi$-electron systems, as indicated by the similarities of the thiocinnamic $\pi$-systems in **1b** and **1c** and the cinnamic $\pi$-systems in **1b** and **1a**, respectively. This is in agreement with the expectation that the contributions of the mesomeric forms of the separate cinnamic systems would be more important than conjugation over the 1,4-diphenyl-1,3-butadiene system. The reduction in the polarization of the $\alpha$-C=$\beta$-C bond in **1b** and **1c** (av $\delta(\beta\text{-C}^X)$-$\delta(\alpha\text{-C}^X)$ = 8.73 ppm in **1b** and **1c** and av $\delta(\beta\text{-C}^Z)$-$\delta(\alpha\text{-C}^Z)$ = 13.76 ppm in **1a** and **1b**) can be attributed to the lower electron-withdrawing power (by induction) of the thiocarbonyl in comparison with a carbonyl group. As the inductive effect decreases rapidly with distance, the increased $\gamma$-effect observed in the thiocinnamic moieties of **1b** and **1c** would be a consequence of the increase in electron withdrawing power by resonance of the thiocarbonyl function. This is also supported by IR studies.

Compounds **1a** and **1c** only show 13 absorptions in the $^{13}C\{^1H\}$ spectrum, which means that these molecules are symmetric in solutions. This is in full agreement with the previously determined crystal structures, which therefore show these compounds to exist exclusively in the *keto* form (i.e., no-$N^+$=C–X– or -$N^+$=C–Z-present). Based on similar N–C(S) and C=S bond distances as well as $^{13}$C chemical shifts, the same would hold for unsymmetrical **1b**.

However, the increasing importance of the contribution of IV in going from **1a** to **1b** to **1c** is clearly demonstrated by the increasingly downfield shift of the N-phenyl carbon atoms in this series. The effect of substitution of the carbonyl with thiocarbonyl group on *i*-$C^Y$ ($\alpha$-effect) is the greatest, followed by *o*-C, while the *meta* positions are the least affected, in accordance with the mesomeric forms involved. This can be explained by the larger positive charge forming on the nitrogen atom as the number of thiocarbonyl groups are increased, due to the stronger resonance electron-withdrawing capability of the sulfur relative to the oxygen. The inductive effect may therefore be considered to be the predominant substituent effect, especially at *i*-C, although the changes in the *o*-C, *m*-C, and *p*-C chemical shifts also reflect resonance effect (see Table 4). The increase in the deshielding resonance effect in the series **1a** → **1b** → **1c**, however, is reduced by the coupled increase in the rotation of the N-phenyl ring (see X-ray structures)

As with other compounds, no significant changes in the chemical shifts of these carbons are observed. However, in going from **1a** to **1b** to **1c**, a downfield shift is observed for all carbons. It is interesting that the shifts for $Ph^X$ in **1b** are slightly more upfield than $Ph^Z$, as the chemical shifts in **1c** are all downfield relative to **1a**.

The $^1J(\beta\text{-C}^X, \beta\text{-H}^X)$ and $^1J(\beta\text{-C}^Z, \beta\text{-H}^Z)$ values varied between 156.7 and 157.3 ppm, and the structural dependence of these values to hybridization effect seems relevant. All other $^1J(C,H)$ coupling constants varied between 160–163 Hz, with the exception of $^1J(o\text{-C}^Y, o\text{-H}^Y)$ of **1a** (164.5 Hz) and **1c** (166.0 Hz).

Both $^2J(C,H)$ and $^4J(C,H)$ couplings were small and relatively unimportant. In contrast, $^3J(C,H)$ couplings were quite large. In all three compounds, the trans vicinal coupling constants $^3J^{tr}(\alpha\text{-C}^X, \beta\text{-H}^Z)$ varied between 10.0 and 10.8 Hz while cis couplings $^3J^{cis}(C(=X), (\beta\text{-H}^X))$ varied between 7.4 and 9.1 Hz. The fact that $^3J^{tr}(C,H) > {}^3J^{cis}(C,H)$ and that the values for $^3J^{tr}$ are more uniform is due to the effect of the different substituents.

## *EXPERIMENTAL*

Melting points are uncorrected. Measurements involved a Gallenkamp melting point apparatus (mp), Bruker IFS 113v FT-IR (IR for dispersion in KBr), Varian-CARY 2390 (UV-vis, in dichloro-methane solutions), and FT Bruker AC 300 spectrometer (NMR in deuteriochloroform solutions). Thin-layer chromatography was carried out on precoated silica gel plates (Merck F254). The solutions were irradiated at 366 nm, using a high pressure mercury lamp (OSRAM 400 Watt, without luminescent phosphorus coating) with a filter (type OX1, Chance Pilkington). Photoreactions were carried out in deuteriochloroform in an appropriate atmosphere in sealed NMR tubes. Light petroleum refers to the fraction boiling in the range 80–100°C.

### (*E*,*E*)-*Dibenzylidene-N-phenylsuccinimide* **1a**

A mixture of (*E*,*E*)-dibenzylidenesuccinic anhydride (5.0 g; 18.1 mmol) and aniline (1.69 g (1.66 ml); 18.1 mmol) in benzene (50 ml) was refluxed for 2 hours. The solvent was removed under reduced pressure, the crude N-phenylsuccinamic acid (6.5 g) was dissolved in acetyl chloride (50 ml), and the solution was refluxed for 2 hours. The excess of acetyl chloride was removed under reduced pressure, and the residue was crystallized from benzene giving the N-phenylimide (5.7 g; 90%) as pale yellow crystals, mp 201.7–202.4°C (turns orange > 117°C), which were suitable for X-ray diffraction studies.

$\lambda_{max}(CH_2Cl_2)$: 337.2 ($\epsilon$ = 12,700), 290.6 ($\epsilon$ = 39.980), 219.8 ($\epsilon$ = 24,800) nm; $v_{max}$: 1764.6 and 1704.3 (C=O), 1625.5, 1597.7, and 1576.0 cm$^{-1}$ (C=C–C=C); detailed $^1$H and $^{13}$C chemical shift assignments of compound **1a** are given in Tables 3 and 4, respectively.

### (*E*,*E*)-*Dibenzylidenesuccinic-N-phenylmonothioimide* **1b** *and -dithioimide* **1c**

2,4-Bis(4-methoxyphenyl)-1,3,2,4-dithiophospentane-2,4-di-sulfide A (Lawesson reagent) was obtained commercially. A mixture of the N-phenylsuccinimide (1.0 g; 2.85 mmol) and the Lawesson reagent (0.58 g; 1.43 mmol) was dissolved in benzene (40 ml) and refluxed for 4 hours with stirring in a dry nitrogen atmosphere. After cooling and evaporation of the solvent, the products were isolated by column chromatography on silica gel using benzene as eluent. The N-phenylmonothioimide was collected as the second fraction and crystallized from benzene-petroleum ether (1:1 v/v) to afford thick yellow-orange needles (0.43 g; 41%), mp 185.1–185.3°C (turns red on melting), suitable for crystal structure determination. The front running fractions yielded the pure N-phen-

**TABLE 5** Crystal Data and Details of Crystallographic Analyses of Compounds **1b** and **1c**

| *Compound* | **1b** | **1c** |
|---|---|---|
| Formula | $C_{24}H_{17}NOS$ | $C_{24}H_{17}NS_2 \cdot CH_3CN$ |
| $M_r$/g · mol$^{-1}$ | 367.5 | 424.6 |
| Spacegroup | $P2_1/c$ | *Pnna* |
| $a$/Å | 8.794(2) | 9.411(2) |
| $b$/Å | 9.623(1) | 17.304(2) |
| $c$/Å | 22.182(5) | 13.574(2) |
| $\beta$/° | 91.45(2) | 90.00 |
| $V$/Å$^3$ | 1876.5 | 2210.5 |
| Z | 4 | 4 |
| $D_x$/g · cm$^{-3}$ | 1.30 | 1.28 |
| $F$(000) | 768 | 888 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 1.44 | 2.13 |
| Scan mode | $\omega:2\theta$ | $\omega:2\theta$ |
| Scan width ($\Delta\omega$)/° | $(0.55 + 0.34 \tan \theta)$ | $(0.45 + 0.34 \tan \theta)$ |
| Aperture/mm | 1.3 × 4.0 | 1.3 × 4.0 |
| Scan range/° | $3 \leq \theta \leq 27$ | $3 \leq \theta \leq 30$ |
| $h$ | $0 \rightarrow 11$ | $0 \rightarrow 13$ |
| $k$ | $0 \rightarrow 12$ | $0 \rightarrow 19$ |
| $l$ | $-28 \rightarrow 28$ | $0 \rightarrow 24$ |
| Reflections collected | 4743 | 3632 |
| $I_{obs}$ ($I > 2\sigma(I)$) | 2524 | 1963 |
| Number of parameters | 296 | 132 |
| Maximum $\Delta\rho/\sigma$ | 0.25 | 0.03 |
| Residual density/eÅ$^{-3}$ | −0.49:0.33 | −0.74:0.75 |
| $R$ | 0.067 | 0.077 |
| $Rw$ | 0.038 | 0.055 |
| Weighting scheme | $\sigma^{-2}$(F) | $\sigma^{-2}$(F) |
| Crystal dimensions/mm | 0.17 × 0.19 × 0.69 | 0.23 × 0.38 × 0.50 |

yldithioimide (0.192 g; 17%) which was crystallized from acetonitrile to give deep red needles, mp 206.4–206.8°C (turns dark red on melting). The dithioimide was isolated in higher yields when a 1 : 1 molar ratio of the imide to the Lawesson reagent was used. The N-phenyldithioimide (0.29 g; 27%) was separated as described previously and the dithioimide collected as deep red needles from acetonitrile with mp the same as given earlier.

*Compound* **1b**. $\lambda_{max}$ ($CH_2Cl_2$): 340.4 ($\epsilon$ = 17,970), 328.6 ($\epsilon$ = 28,870), 296.0 ($\epsilon$ = 19,570), 237.4 ($\epsilon$ = 17,380) nm; $v_{max}$: 1730.34 (C=O), 1133.47 (C=S), 1625.24, 1595.35, 1573.17 $cm^{-1}$ (C=C–C=C).

*Compound* **1c**. $\lambda_{max}$ ($CH_2Cl_2$): 402.2 ($\epsilon$ = 13,840), 355.0 ($\epsilon$ = 25,600), 242.6 ($\epsilon$ = 18,170) nm; $v_{max}$: 1157.10, (1146.97 sh), 1132.51 (C=S), 1617.04, 1593.90, 1571.72 $cm^{-1}$ (C=C–C=C)

The $^1H$ and $^{13}C$ chemical shift values of compounds **1b** and **1c** are given in Tables 3 and 4, respectively.

## CRYSTALLOGRAPHIC ANALYSIS

Relevant crystallographic data and details of the single-crystal analysis of compounds **1b** and **1c** are given in Table 5. Diffraction quality crystals of **1b** and **1c** were obtained by crystallization from acetonitrile.

Diffraction intensities were measured at room temperature with an Enraf Nonius CAD4 diffractometer, using graphite monochromated Mo-K$\alpha$ radiation ($\lambda$(Mo-K$\alpha$) = 0.71073 Å). Cell constants were obtained by fitting the setting angles of 25 high-order reflections. The stability of the crystal was tested every hour with three control reflections and the orientations tested every 200 reflections.

A $\omega/2\theta$ scan with a variable speed was used for all compounds. The $\omega$-angle changed as $a_w + b_w \tan \theta$. The horizontal aperture was fixed to 1.3 mm, and the vertical slit to 4 mm. Optimal values of $a_w$ and $b_w$ were determined for each crystal by a critical evaluation of peak shape and peak/noise ratios of several reflections at different values of $\theta$.

Where applicable, a linear decay correction was applied using the mean value of linear curves fitted through three intensity control reflections measured at regular time intervals. Data were corrected for Lorentz and polarization effects and for absorption by an empirical method [22]. Direct methods [23] and subsequent Fourier analysis revealed the position of all nonhydrogen atoms, which were refined anisotropically with SHELX76 using a $\sigma_F^2$-weighted full matrix scheme [24] until no significant shift occurred. All hydrogen atoms were either located from subsequent Fourier maps or were placed on their expected positions. In the latter case the hydrogen atoms were forced to ride upon their associated non-hydrogen atoms. Hydrogens were refined with a common isotropic temperature factor. The dithioimide **1c** was found to co-crystallize with a disordered acetonitrile solvent molecule [25].

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