The *N*-(1-phenylethyl)dithiocarbamate anion. Electronic transitions, ultraviolet and CD spectra, and reversible formation of its ammonium salts

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The UV and CD spectra of tetrabutylammonium (*S*)-*N*-(1-phenylethyl)dithiocarbamate (**3c**) have been recorded in acetonitrile and in absolute ethanol. In the dithiocarbamate anion, the sulfur lone pairs are expected to interact to give a low-energy symmetric combination (n_+) and an antisymmetric combination (n_-) with the higher energy. The UV spectrum was interpreted with the aid of CNDO/S calculations, and the CD spectrum with calculations by the Schellman matrix method. The CD spectrum contains a medium-strong positive band at 230 nm, which lacks a counterpart in the UV spectrum and was initially tentatively assigned to the $n_+ \rightarrow \pi_1^*$ transition. However, the theoretical calculations predict a negative sign for this band, and consequently no assignment for the 230 nm band can be given at present.

Except for the 230 nm band, the calculations predict correct signs and qualitatively correct intensities for the CD bands between 200 and 400 nm in a narrow range of orientations of the 1-phenylethyl group with respect to the dithiocarbamate ion, and it is expected that the favoured conformation falls in this conformational range.

Similar studies of (*S*)-(1-phenylethyl)ammonium (*S*)-*N*-(1-phenylethyl)dithiocarbamate (**3a**) and triethylammonium (*S*)-*N*-(1-phenylethyl)dithiocarbamate (**3b**) failed because these salts decompose in solution with ultimate formation of carbon disulfide. This decomposition has been studied by UV spectroscopy, and a mechanism has been proposed.

Introduction

In his extensive study of the UV spectra of organic thiocarbonyl compounds, Janssen[1–4] included some sodium dithiocarbamates based on primary and secondary aliphatic amines (*e.g.* **1**, **2**, Scheme 1). The spectra in ethanol showed one weak band (ε = 60–80) near 350 nm and stronger bands (ε = 12 000–18 000) at 288 and 253 nm respectively.[1] The bands were interpreted with the aid of SCF calculations of Hückel type as an $n \rightarrow \pi^*$ and two $\pi \rightarrow \pi^*$ transitions. Janssen noted that the two sulfur lone pairs interact to give a symmetric and an antisymmetric combination (n_+ and n_-, Fig. 1), and consequently two $n \rightarrow \pi^*$ transitions to the lowest π^* level can be expected, the one observed being the $n_- \rightarrow \pi^*$ transition. Multiple $n \rightarrow \pi^*$ transitions have previously been observed in 1,2- and 1,3-dithiones, and up to four bands assignable to $n \rightarrow \pi^*$ transitions were observed in UV spectra of tetrathiooxalates[5] and in CD spectra of chiral dithiooxamides.[5,6]

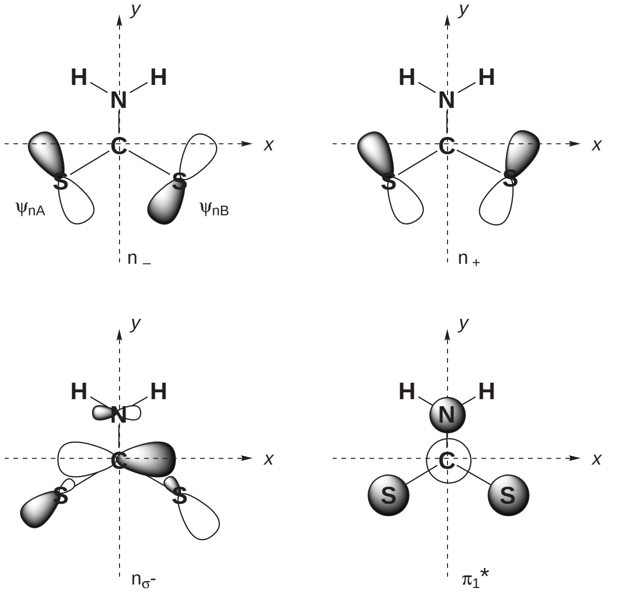


Fig. 1 Orbital schemes for $H_2NCS_2^-$.

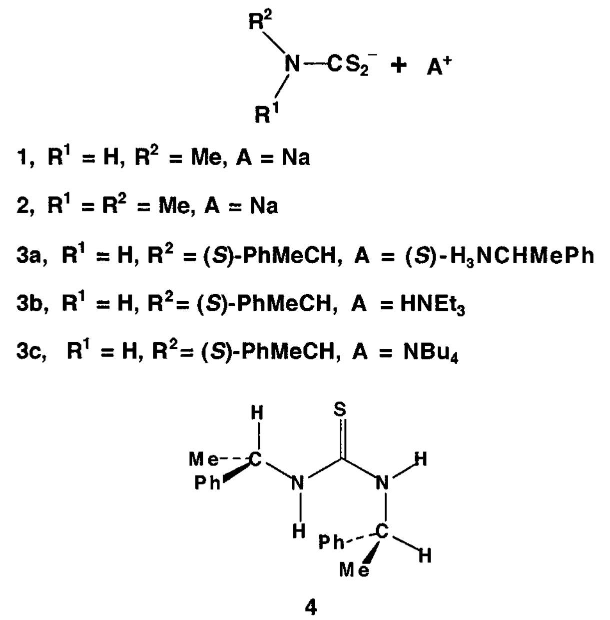
CD spectroscopy is a useful technique to locate and identify "hidden" $n \rightarrow \pi^*$ transitions, when the corresponding UV bands are overlapped by stronger $\pi \rightarrow \pi^*$ bands. Thus the carbonyl $n \rightarrow \pi^*$ transitions could be located in the CD spectra of chiral rhodanines containing the *N*-acyldithiocarbamate chromophore.[7,8] Hoping to locate the $n_+ \rightarrow \pi^*$ transition in the dithiocarbamate anion and to obtain information about the polarization of the $\pi \rightarrow \pi^*$ transitions, we have studied UV and CD spectra of chiral dithiocarbamates of type **3** (Scheme 1). To be able to record spectra in non-hydroxylic solvents we chose to study dithiocarbamates with lipophilic cations. We have recently described *N*-(1-phenylethyl)ammonium *N*-(1-phenylethyl)dithiocarbamate (**3a**),[8] which is soluble in acetonitrile. In order to avoid contributions to the CD spectrum from the cation, we have now prepared triethylammonium and tetrabutylammonium dithiocarbamate (**3b** and **3c**). It was observed that **3b** underwent decomposition in ethanol and acetonitrile solution, whereas solutions of **3c** were stable.

In the following the UV and CD spectra of **3c** and the mechanism for the decomposition of **3b** will be discussed.

Experimental

Preparations

Triethylammonium (*S*)-*N*-(1-phenylethyl)dithiocarbamate (3b). A solution of carbon disulfide (0.38 g, 0.005 mol) in dry Et_2O (5 ml) was added with stirring at 0 °C to a solution of (*S*)-1-phenylethylamine (0.61 g, 0.005 mol) and triethylamine (0.51 g, 0.005 mol) in dry Et_2O (10 ml). A crystalline precipitate



Scheme 1

appeared immediately and was separated by filtration after storage for 24 h at −20 °C (1.22 g, 82%), mp 70 °C (Heizbank). δ_H ($CDCl_3$, 300 MHz) 1.377 (tripl., 9H, $J = 7.3$ Hz), 1.50 (broad, 1H), 1.538 (d, 3H, $J = 7.0$ Hz), 3.279 (quart., 6H, $J = 7.3$ Hz), 5.633 (quint., broad, 1H, $J = 7$–8 Hz), 7.14–7.40 (m, 5H), 7.80 (broad d, 1H, $J \approx 8$ Hz).

Tetrabutylammonium (*S*)-*N*-(1-phenylethyl)dithiocarbamate (3c). Tetrabutylammonium hydrogen sulfate (3.4 g, 0.01 mol) was dissolved in 11 ml 1 M aqueous sodium hydroxide solution in a separatory funnel. (*S*)-(1-Phenylethyl)amine (1.21 g, 0.01 mol) and carbon disulfide (0.76 g, 0.01 mol) in trichloroethene (15 ml) were added. The funnel was shaken vigorously several times during 1 h. The organic phase was separated, washed with water, dried and evaporated, leaving a clear, viscous, non-crystallizable yellow oil (3.81 g, 87% yield). δ_H ($CDCl_3$, 500 MHz) 0.880 (tripl., 12H, $J = 7.4$ Hz), 1.307 (sext., 8H, $J = 7.4$ Hz), 1.404 (d, 3H, $J = 6.9$ Hz), 1.514 (quint., 8H), 3.166 (m, 8H), 5.70 (quint., 1H, $J \approx 7$ Hz), 7.07–7.35 (m, 5H), 7.62 (broad d, 1H, $J \approx 7$ Hz). δ_C ($CDCl_3$, 125 MHz) 13.656 ($\mathit{C}H_3CH_2$), 19.679 ($CH_3\mathit{C}H_2$), 21.695 ($\mathit{C}H_3CHPh$), 24.021 ($\mathit{C}H_2CH_2N$), 55.540 ($CH_3\mathit{C}HPh$), 58.722 ($CH_2\mathit{C}H_2N$), 125.333 (C_{para}), 126.435 (C_{ortho}), 128.129 (C_{meta}), 128.379 (C_{ipso}), 214.592 ($N\mathit{C}S_2$). FAB-MS (*m*/*z*, % rel. int. Only peaks with intensity >20% are reported), negative ion mode: 228 (100, $C_9H_{10}NS_2^- + O_2$), 196 (72, $C_9H_{10}NS_2^-$), 153 (27). Positive ion mode: 242 (100, $C_{16}H_{36}N^+$).

The NMR samples of **3b** and **3c** in chloroform-*d* are unstable because of reaction of the dithiocarbamate anion with the solvent, and the NMR spectra had to be recorded without delay. For the same reason dichloromethane and chloroform could not be used as solvents in the ion pair extraction of **3c**.

Spectroscopy

The ^1H NMR spectrum of **3b** was recorded with a Varian XL-300 spectrometer operating at 299.94 MHz at ambient temperature (*ca.* 300 K). the ^1H and ^{13}C NMR spectra of **3c** were recorded with a Bruker ARX 500 NMR spectrometer operating at 500.14 MHz at the same temperature. FAB mass spectra in the positive and negative ion modes were obtained with a JEOL JMS-SX 102 mass spectrometer operating at an accelerator voltage of 8 kV with a mass range of 0–3000. The instrument was equipped with a standard JEOL FAB source and an ion gun (Xe atom beam). Spectra were obtained with a magnet scan rate of 5 s scan^{-1} and the data were processed with a JEOL JMA 5000 data processing system. UV spectra were recorded with a Cary Model 2290 spectrophotometer, By using 0.1 cm cells, it was possible to record spectra down to 190 nm. CD spectra were recorded with a JASCO Model J-500A spectropolarimeter. The experimental spectra were digitized and simulated by a set of Gaussians, using a least squares approach.[9] Quite good agreement with the experimental curves was obtained. From the Gaussians, the rotational strengths of the transitions (R_i, in Debye·Bohr magnetons) were obtained from eqn. (1), where Δ_e is half the bandwidth at $\Delta\varepsilon = \Delta\varepsilon_{max}/e$.

$$R_i = 0.4389\Delta\varepsilon_{max}\Delta_e/\lambda_{max} \qquad (1)$$

Calculations

CNDO/S calculations were performed on the unsubstituted dithiocarbamate anion with a program based on the original Jaffé formalism but modified for sulfur compounds by Pfister-Guillouzo and co-workers.[10] Two-center repulsion integrals were calculated by the Nishimoto–Mataga formalism,[11] and configuration interaction was performed with the 20 lowest singly excited states. Inclusion of a larger number of configurations has only a moderate effect on the calculated transition energies and oscillator strengths and it complicates the analysis of the transitions in terms of molecular orbitals. Calculations were performed with and without d orbitals for sulfur in the basis set, giving qualitatively rather similar transition energies.

An idealized geometry for the unsubstituted dithiocarbamate anion for this calculation was created as an average of structural data from crystallographic studies of simple lithium and sodium dithiocarbamates.[12–16] The C–S bonds were given the same length, 172.0 pm, the C–N bond 133.5 pm, and the N–H bonds 102 pm. All bond angles were 120°. The same geometry was used, with the aid of the MacMimic implementation[17] of the Allinger MM2-91 force field,[18] to model the *N*-(1-phenylethyl)dithiocarbamate anion. Due to lack of force-field parameters, no attempt was made to minimize the energy of this anion.

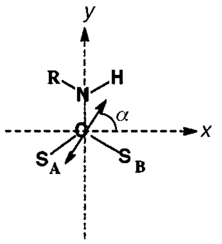
AM1 calculations[19] were performed with the MacSpartan Plus program package.[20] The calculated geometries deviate to some extent from those derived from the crystal structures, the C–S bonds being predicted to be *ca.* 165 pm and the $(S_2)C$–N bond 138.5 pm. The calculations were used to derive static charges and conformational energies.

Theoretical calculations of the CD spectra were performed with the matrix technique devised by Schellman and co-workers.[21–24] The calculations involve the n→π* and the π→π* transitions in the dithiocarbamate anion and the π→π* transitions in the phenyl chromophore. The required input is transition energies, strengths and directions of electric and magnetic transition dipoles, transition monopoles, and finally static charges for the atoms outside the chromophore plane. The methods for derivation of these data have recently been summarized,[25] and the results for the dithiocarbamate anion are shown in Table 1. The data for the benzene ring were published earlier.[7]

Results and discussion

The UV spectrum of the tetrabutylammonium dithiocarbamate **3c** (Fig. 2 and Table 2) in methanol solution displays a weak band at 340 nm, stronger bands at 290 and 254 nm and a shoulder at 205 nm. The corresponding CD spectrum (Fig. 3 and Table 2) shows bands in the same regions, a broad and weak positive band at 342 nm (band A), a moderately strong positive band at 293 nm (band B), and a negative band of similar intensity at 255 nm (band C). Three sharp positive bands at 272, 265 and 258 nm and a broader positive band (band D) at 230 nm are without observable counterparts in the UV spectrum. A positive CD band at 210 nm probably corresponds to the

Table 1 Input data for the theoretical calculation of the CD spectra of **3c**[a]

Chromophore	ν/kK[b]	μ[c], m[d]	α/°	Transition charges	Transition
	27.62	0.3949[d]	30	0.450 ($x,y = \pm 0.621$)[e]	$n_{-}\rightarrow\pi_1^*$ (A)
	33.06	3.03[c]	0	$S_{A,B}$: ±0.1103	$\pi_1\rightarrow\pi_1^*$ (B)
	38.91	3.35[c]	90	$S_{A,B}$: +0.1261 C: −0.1503 N: −0.1018	$\pi_2\rightarrow\pi_1^*$ (C)

[a] The charges are in units of the protonic charge. [b] 1 kK = 10^3 cm^{-1}. [c] Electric transition moment in D. [d] Magnetic transition moment in Bohr magnetons, for a transition in a single S–C bond. [e] Transition quadrupole on the sulfur atom, in the x,y plane in a local coordinate system with the z axis along the C–S bond.

Table 2 Ultraviolet and circular dichroism spectra of tetrabutylammonium *N*-(1-phenylethyl)dithiocarbamate (**3c**)

Solvent	λ/nm (ε, $\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1})
Acetonitrile (UV)	362 (860, A), 303 (12 200, B), 257 (11 800, C), 205 S[a] (23 100)
Acetonitrile (CD)	370 (+0.19, A), 303 (+2.05, B), 272.5 (−0.19), 265 (−1.40), 258 (−3.05, C), 230 (+0.84, D), 210 (+1.3)
Methanol (UV)	340 (970, A), 290 (9500, B), 254 (11 200, C), 205 S (22 000)
Methanol (CD)	342 (+0.35, A), 293 (+2.64, B), 272.5 (−0.58), 265 (−1.70), 255 (−3.69, C), 230 (+2.99, D), 210 (+2.1)

[a] Shoulder.

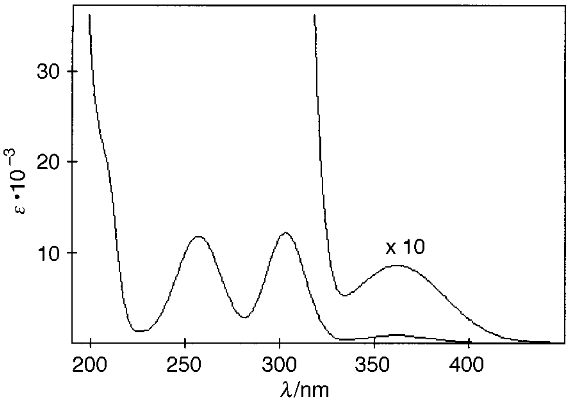


Fig. 2 Ultraviolet spectrum of **3c** in methanol.

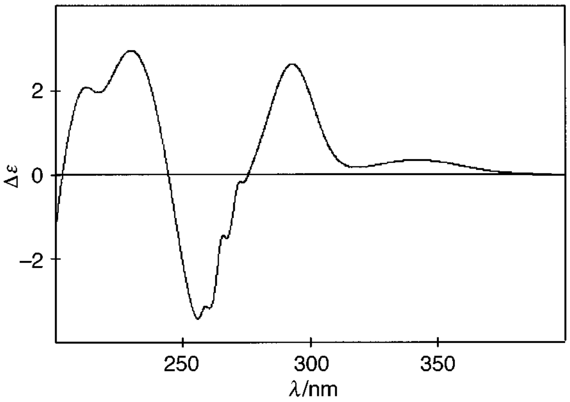


Fig. 3 CD spectrum of **3c** in methanol.

shoulder at 205 nm in the UV spectrum. This is followed by a negative band, but due to strong UV absorption in combination with low g values the CD spectrum could not be recorded at wavelengths below 200 nm.

Table 3 UV spectral data calculated by the CNDO/S method

	λ/nm	f[a]	Polarization[b]	Assignment
Without d orbitals	447.6	0.000	—	$n_{-}\rightarrow\pi_1^*$
	286.5	0.000	—	$n_{+}\rightarrow\pi_1^*$
	281.1	0.112	x	$\pi_1\rightarrow\pi_1^*$
	228.3	0.000	—	$n_{\sigma}\rightarrow\pi_1^*$ (antisymmetric n_{σ} combination)
	212.7	0.090	y	$\pi_2\rightarrow\pi_1^*$
With d orbitals	492.8	0.000	—	$n_{-}\rightarrow\pi_1^*$
	321.0	0.000	—	$n_{+}\rightarrow\pi_1^*$
	298.2	0.158	x	$\pi_1\rightarrow\pi_1^*$
	223.7[c]	0.099	y	$\pi_2\rightarrow\pi_1^*$

[a] Oscillator strength. [b] See Fig. 1. [c] Five forbidden transitions are predicted between 270 and 226 nm.

The UV and CD spectra of **3c** in acetonitrile solution are similar, but bands A, B and C are shifted bathochromically.

Band A agrees in energy with the $n_{-}\rightarrow\pi^*$ band observed by Janssen,[1,4] but its intensity in the UV spectrum is an order of magnitude higher. This may be due to homoconjugation with the phenyl group, as discussed for 5-phenylrhodanines.[7] Bands B and C agree with those designated as type II and type III by Janssen. Of these, only the former was assigned to a $\pi\rightarrow\pi^*$ transition while the origin of the type III bands was left open. Based on the results of the CNDO/S calculations discussed below, band C can safely be assigned to a second $\pi\rightarrow\pi^*$ transition. The sharp bands between 258 and 272 nm are most likely due to the ^1L_b ($^1A\rightarrow{}^1L_b$) transition[26] in the benzene chromophore, which normally shows vibrational fine structure. The shoulder seen in the UV spectrum at 205 nm and the positive CD band at 210 nm are assigned to the benzene ^1L_a transition. It is tempting to assign band D to the $n_{+}\rightarrow\pi^*$ transition. At first sight the insensitivity of its position to solvent polarity (Table 2) may speak against this interpretation, since band A, as expected, shows a strong hypsochromic shift when going from acetonitrile to methanol as solvent. However, in some of the systems containing two $n\rightarrow\pi^*$ transitions, *e.g.* dithiosuccinimides and dithioglutarimides,[27] the low-energy combination, $n_{-}\rightarrow\pi^*$, shows a strong hypsochromic shift with increasing solvent polarity, while the transition at higher energy, $n_{+}\rightarrow\pi^*$, shows a very small hypsochromic shift. For dimethyl dithiooxalate even a small bathochromic shift is observed.[5] Evidently, the solvent effect, which is so diagnostic for simple $n\rightarrow\pi$[28] and $n_{-}\rightarrow\pi^*$ transitions is not useful for $n_{+}\rightarrow\pi^*$ transitions.

CNDO/S calculations on the unsubstituted dithiocarbamate anion (Table 3) predict two forbidden $n\rightarrow\pi^*$ transitions, originating in the lone pair combinations n_{-} and n_{+}, followed by an allowed $\pi\rightarrow\pi^*$ transition, polarized along the x axis (Fig. 1). After a forbidden transition (designated as $n_{\sigma-}\rightarrow\pi^*$, *vide infra*) follows a second allowed $\pi\rightarrow\pi^*$ transition, polarized along the *y* axis. As is common in CNDO/S calculations on thiones,[5] the energy of the n→π* transition is vastly underestimated.

The splitting of the $n_-\rightarrow\pi^*$ and $n_+\rightarrow\pi^*$ transitions is predicted to be 12 600 cm^{-1}, much larger than for 1,2-dithiones (calculated 1300–2400 cm^{-1}, experimental value 1450 cm^{-1})[5] or 1,3-dithiones (calculated 400–1000 cm^{-1}, no splitting observed[29]). If we assign band D to the $n_+\rightarrow\pi^*$ transition, the experimental splitting in **3c** is 15 900 cm^{-1}. Evidently, the results of the calculations are in qualitative agreement with this assignment.

Theoretical calculation of CD spectra

Calculation of CD spectra by the Schellman method[21] combines the Condon–Altar–Eyring (CAE),[30] the magnetic–electric coupling[31,32] and the coupled oscillator[33] mechanisms. In the CAE mechanism one n→π* and one π→π* transition in the same planar chromophore are "mixed" by chirally placed static charges outside the plane of the chromophore. The application of the program to **3c** is complicated by the fact that we need to consider two n→π* and two π→π* transitions in the dithiocarbamate anion chromophore, while the program permits only one n→π* and one π→π* transition in each chromophore with the CAE mechanism and only one n→π* transition in the magnetic–electric coupling mechanism. In the dithiocarbamate anion, the n→π* transitions originate in the antisymmetric (ψ_{n-}) and symmetric (ψ_{n+}) combinations of the sulfur lone pair orbitals (ψ_{nA} and ψ_{nB}, Fig. 1) and the treatment has to be modified. The rotational strengths of one n→π* transition can be expressed by eqn. (2),[32] where *V*, the first order perturbation energy, is the energy of interaction between the transition quadrupole related to the n→π* transition and the chirally placed static charges, q_i. $v_{\pi\pi^*}$ and $v_{n\pi^*}$ are the respective transition energies, and $m_{n\pi^*A}$ and $m_{n\pi^*B}$ are the magnetic transition

$$\mathbf{R}_{n\rightarrow\pi^*} = -V\cdot\mu_{\pi\pi^*}\cdot m_{n\pi^*}/(v_{\pi\pi^*} - v_{n\pi^*}) = -\mathbf{R}_{\pi\rightarrow\pi^*} \qquad (2)$$

$$\psi_{n\pm} = (2)^{-0.5}(\psi_{nA} \pm \psi_{nB}) \qquad (3)$$

$$V = <\psi_n|\Sigma q_i/r_i|\psi_{\pi^*}> = (2)^{-0.5}(<\psi_{nA}|\Sigma q_i/r_{i'}|\psi_{\pi^*}> \pm <\psi_{nB}|\Sigma q_i/r_{i''}|\psi_{\pi^*}>) \qquad (4)$$

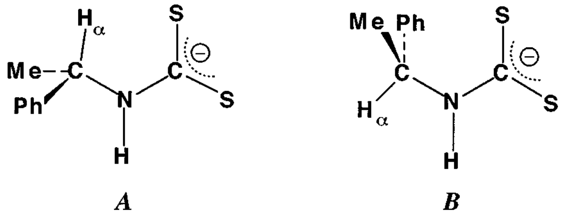
$$m_{n\pi^*} = m_{n\pi^*A} \pm m_{n\pi^*B} \qquad (5)$$

moments corresponding to the respective transitions from ψ_{nA} and ψ_{nB} to the π* orbital. The latter moments are vectors oriented along the respectives S–C bonds. Since the lobes of π_1^* on the sulfur atoms are in the same phase (Fig. 1), the individual magnetic moments have the same direction along the C–S bonds in the $n_-\rightarrow\pi^*$ transition and opposite directions in the $n_+\rightarrow\pi_1^*$ transitions, and the resultant magnetic transition moment is *y*-oriented in the former and *x*-oriented in the latter case. Since the $\pi_1\rightarrow\pi_1^*$ transition is *x*-polarized and the $\pi_2\rightarrow\pi_1^*$ is *y*-polarized (Table 1), the scalar product $\mu_{\pi\pi^*}\cdot m_{n\pi^*}$, and thus also $\mathbf{R}_{n\rightarrow\pi^*}$, vanishes for the $n_-\rightarrow\pi_1$–$\pi_1^*\rightarrow\pi_1^*$ and $n_+\rightarrow\pi_1^*$–$\pi_2\rightarrow\pi_1^*$ interactions.

However, the magnetic–electric coupling[31,32] also contributes to $\mathbf{R}_{n\rightarrow\pi^*}$. An expression similar to eqn. (2) has been given for the contribution from one n→π*–π→π* interaction.[32] In this case, $\mu_{\pi\pi^*}$ is an electric transition moment in a different, chirally placed chromphore (an "external" chromophore), in **3c** the phenyl ring, and the perturbation energy, *V*, is the energy of interaction between $\mu_{\pi\pi^*}$ and the n→π* transition quadrupole. Similar contributions arise from all interactions of π→π* transitions in "external" chromophores with the n→π* transitions in the "central" chromophore.

Using the Schellman method with appropriate combinations of transitions, it is possible to calculate the terms from the $n_-\rightarrow\pi_2^*$ and $n_+\rightarrow\pi_1^*$ transitions arising from the CAE and mμ mechanisms, which contribute to the rotational strengths. Calculation of the contributions from the coupled oscillator mechanism is straightforward.

For these calculations, it is necessary to know the geometry of **3c** in solution. In a recent work,[34] we have studied the structure of *N*,*N'*-bis[(*S*)-(1-phenylethyl)]thiourea (**4**), which has some structural similarity to **3c**. As for all secondary alkyl groups attached to planar frameworks, the two main conformational types *A* and *B* (Scheme 2) need to be considered.[35–37] It was shown that the conformer of **4** corresponding to *B* is strongly disfavoured by steric and coulombic repulsion between the aromatic ring and the sulfur atom.[34,37] The negative charge in **3c** must increase this repulsion both by making the electron cloud around the sulfur atom more diffuse and by augmenting the coulombic repulsion between the sulfur atom and the negatively charged aromatic carbon atoms. Consequently, only conformer *A* needs to be considered. However, force-field calculations on **4** indicated the existence of several close-lying energy minima, forming what was called a "conformational family", differing in the value of the H_α–C–N–C dihedral angle (*a*). The globe energy minimum was found at *a* = −35°.



Scheme 2

AM1 geometry optimizations of the *N*-(1-phenylethyl)-dithiocarbamate anion, starting with *a* = 0° (*A*) and 180° (*B*) led to energy minima with *a* = −9.6 and −164.7° respectively, the former being 10.2 kJ mol^{-1} lower in energy.

Calculations by the Schellman method were performed for *a* values in steps of 10° from *a* = +40° to *a* = −40°, which should include all feasible values for *a* in the *A* family. One calculation was performed for *a* = 180°, corresponding to the *B* conformation (Table 4). The phenyl ring was oriented with respect to the C_α–N bond approximately as in the *Za* part of bis[(*S*)-(1-phenylethyl)]thiourea, with the C_{ortho}–C_{ipso}–C_α–N dihedral angles = −60 and +120°. Very similar angles were found in the AM1 optimized geometries.

Comparison of the experimental rotational strengths with the calculated ones shows good agreement in the range −40° ≤ *a* ≤ −20° except for the transition assigned as $n_+\rightarrow\pi_1^*$ (D). Positive rotational strengths for this transition are predicted only for *a* = +40 and 180°, but for these conformations the wrong signs are predicted for transitions A, B and ^1B_b, and at 180° also for C and ^1L_b. The good agreement in sign and order of magnitude for six transitions in the range −40° ≤ *a* ≤ −20° gives good support for the assumption that the molecules preferentially reside in this range.

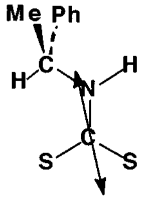
Different explanations may be advanced for the incorrectly predicted sign for band D. One may be that the assumption of strictly *x* and *y* polarized π→π* transitions is an oversimplification. Homoconjugation with the phenyl ring may change the polarization directions and *e.g.* allow interaction between an electrically nearly *y*-polarized $\pi_2\rightarrow\pi_1^*$ and a magnetically *x*-polarized $n_+\rightarrow\pi_1^*$ transition. In a model calculation combining these two transitions with the CAE mechanism, the electric moment was rotated 15 degrees from the (S_2)C–N direction in the direction of the substituent (Scheme 3). However, the resultant rotational strengths were only 4% of those required and with the wrong signs. Apparently, this is not a feasible explanation.

Another explanation for the incorrect prediction of the sign for band D may be that the corresponding transition has not been correctly assigned, *i.e.* it is not the $n_+\rightarrow\pi_1^*$ transition.

Table 4 Experimental rotational strengths ($\mathbf{R}^a$) and theoretical values as a function of the H_α–C_α–N–C dihedral angle (α)

Transition	$n_- \to \pi_1^*$ A	$\pi \to \pi_1^*$ B	$\pi \to \pi_2^*$ C	($n_+ \to \pi_1^*$) D	^1L_b	^1L_a	^1B_b	^1B_a
Experimental values	+0.0112	+0.048	−0.076	+0.086	+0.0056	+0.022	<0	—
α/°								
−40	+0.0435	+0.1189	−0.0768	−0.0680	+0.0036	+0.0229	−0.0285	+0.0204
−30	+0.0261	+0.0984	−0.0942	−0.0533	+0.0031	+0.0333	−0.0211	+0.0297
−20	+0.0156	+0.0789	−0.1152	−0.0485	+0.0028	+0.0421	−0.0111	+0.0376
−10	+0.0103	+0.0746	−0.1377	−0.0512	+0.0022	+0.0489	+0.0016	+0.0437
0	−0.0240	+0.0225	−0.1240	−0.0455	−0.0016	+0.0627	+0.0212	+0.0512
+10	+0.0059	+0.0737	−0.1759	−0.0649	+0.0009	+0.0537	+0.0352	+0.0482
+20	−0.0007	+0.0615	−0.1831	−0.0597	+0.0002	+0.0500	+0.0565	+0.0453
+30	−0.0375	+0.0207	−0.1731	−0.0185	−0.0046	+0.0207	+0.1326	+0.0175
+40	−0.0706	−0.1075	−0.1275	+0.0715	+0.0004	+0.0229	+0.1025	+0.0225
180	−0.1807	−0.3908	+0.1133	+0.1828	−0.0378	−0.0036	+0.1281	−0.0031

[a] In Debye·Bohr magnetons (D·BM). 1 D·BM = $3.0917 \cdot 10^{-53}$ SI units = $9.2741 \cdot 10^{-39}$ cgs units.



Scheme 3

Since no corresponding band is apparent in the UV spectrum, a $\pi \to \pi^*$ transition of sufficient strength to give rise to the fairly strong CD band at 230 nm is unlikely. Based on *ab initio* random phase calculations, Kajtar *et al.*[38] have proposed a transition described as $n_\sigma \to \pi^*$ to be responsible for an absorption band frequently observed near 220 nm in UV and CD spectra of simple thioamides. The n_σ orbital is described as a lone pair with some C–S σ character. Similar orbitals, in symmetric and antisymmetric combinations, can be expected in the dithiocarbamate anion, and the D band could be due to an $n_\sigma \to \pi^*$ type of transition. Our CNDO/S calculation excluding d orbitals actually predicts a transition of this kind at 228 nm (Table 3), originating in an antisymmetric combination of n_σ orbitals ($n_{\sigma-}$, Fig. 1).

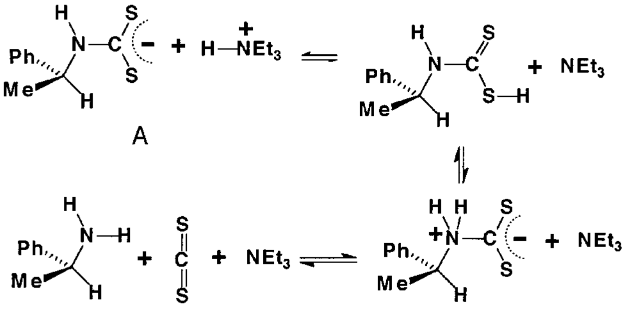
Unfortunately, the program used for theoretical calculations of CD spectra cannot handle this kind of transition, and we have to leave open the question of the nature of the transition responsible for the D band and also the energy of the true $n_+ \to \pi_1^*$ transition.

The inclusion of a "false" $n_+ \to \pi_1^*$ transition with negative rotational strength in calculations reported in Table 4 leads to the appearance of spurious positive rotational strengths for the other transitions, notably for $\pi_1 \to \pi_1^*$. A correction for this gives values for $\mathbf{R}(\pi_1 \to \pi_1^*)$ closer to the experimental ones and with correct sign.

Summing up, the theoretical calculations of rotational strengths (Table 4) support the view that the 1-phenylethyl group in **3c** assumes a conformation of type *A* (Scheme 2) with a H_α–C–N–C dihedral angle in the range −20 to −30°. No assignment of the transition responsible for band D is possible.

Behaviour of triethylammonium (*S*)-*N*-(1-phenylethyl)dithiocarbamate (3b) in solution

The UV spectrum of **3b** in acetonitrile initially resembles that of **3c**, but the intensity diminishes gradually to a limiting value, while at the same time a strong, narrow (Δ_e = 7.5 nm) UV band appears at 206 nm with gradually increasing intensity. The latter band with all probability is due to carbon disulfide, formed in the reaction sequence shown in Scheme 4. A UV spectrum of carbon disulfide in absolute ethanol displays one single Gaussian band at 206.5 nm with ε = 74 800 and Δ_e = 7.2 nm, corresponding to an oscillator strength (f) of 0.97. Earlier authors[39] report a band in cyclohexane at 209.7 nm with f = 0.558.



Scheme 4

The CD spectrum of **3b** shows a similar behaviour, and the strong absorption of carbon disulfide precluded measurements at wavelengths shorter than 210 nm. The same results were found with solutions in ethanol. In both solvents the UV spectra passed through isosbestic points at 215 and 192 nm, indicating a clean conversion according to Scheme 4.

Plots of the logarithms of the UV absorbances of bands 2 or 3 *versus* time initially showed nearly linear behaviour, but gradually the plot showed increasing curvature towards the time axis, in agreement with the reversibility of the reaction. In 2×10^{-4} M solutions, the equilibrium was reached after 80–85% conversion in acetonitrile and ethanol solution with apparent halflives of 120 and 160 min respectively at 20 °C. On prolonged reaction times a secondary reaction became noticeable, indicated by the reduction of the carbon disulfide absorption. It may quite possibly be formation of *N*,*N*′-bis[(*S*)-1-phenylethyl]-thiourea (**4**), which has been shown to be formed by decomposition of **3a**,[34] for which the requisite components are present in the reaction mixture. The presence of **4** is supported by the appearance of an absorption band at *ca.* 250 nm, the position of the first strong absorption band of **4**,[34] after a reaction time of 24 h.

In water solution the conversion was only *ca.* 5%. This difference can be rationalized by the better stabilization of the ions (A, Scheme 4) by water than by ethanol or acetonitrile. Solutions of the tetrabutylammonium dithiocarbamate **3c** in ethanol and acetonitrile showed normal stability, as expected. The decomposition of the dithiocarbamate anion in the presence of an acidic ammonium ion is analogous to the one undergone by alkali dithiocarbamates in acid medium, leading to amine and carbon disulfide.[40]

Studies of the UV and CD spectra of the dithiocarbamates in non-polar solvents like cyclohexane were precluded by low solubility. Attempts to increase the solubility by addition of dichloromethane or chloroform led to reaction of the strongly nucleophilic dithiocarbamate anions with this solvent with concomitant strong, time-dependent changes of the spectra.

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