Preparation, Chromatographic Enantiomer Separation, Ultraviolet–Visible and Circular Dichroism Spectra, and Barriers to Rotation of Chiral Twisted 1-Acyl-1-thioacyl- and 1,1-Bis(thioacyl)-2,2-diaminoethylenes

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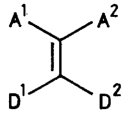
Three 1-acyl-1-thioacyl-2,2-diaminoethylenes and three dithio analogues with the amino groups included in a six-membered ring and carrying unlike groups (Pr^i and $PhCH_2$) have been prepared by thiation of the oxygen analogues. These compounds are strongly twisted about the double bond, and four of them with unlike (thio)acyl groups are chiral and have been preparatively resolved by chromatography on swollen, microcrystalline triacetylcellulose. C.d. spectra have been recorded, and free energy barriers to rotation through the planar state (123—127 kJ mol^{-1}) have been determined by monitoring the thermal racemization. Owing to the twist about the formal double bond, the compounds are best described as internal amidinium 1-(thio)acylvinyl-2-thiolates, and the electronic transitions are interpreted with the aid of CNDO/S calculations to occur partly in the (thio)acylvinylthiolate group, partly as charge transfer between this and the amidinium group. The latter transitions are made possible by overlap between the thiocarbonyl lone pair orbitals and the π^* orbital in the amidinium group.

It has been known for some time[1] that push–pull ethylenes, *i.e.* ethylenes carrying electron-accepting groups on one carbon atom and donors on the other (**1**), may have quite low barriers to rotation about the C=C bond. In systems where the donor and acceptor parts are sterically demanding, non-bonding interactions between them may be released by rotation about the C=C bond. The twist angle is determined by the balance between steric and electronic effects (Figure), and molecules are known in which the barriers to passage of the perpendicular and planar states are of similar height[2,3] (Figure a), and others in which the donor (D^1–C–D^2) and acceptor (A^1–C–A^2) parts are nearly perpendicular, and the barrier to passage of the planar state is the only detectable one (Figure b). A compound with a twist angle of 80.8° in the crystal has recently been described (**2**).[4] In this and similar systems, the 'double' bond is quite long (*ca.* 1.48 Å), and the molecules are best described as zwitterionic.

Several compounds have been prepared, in which the barrier to passage through the planar state is *ca.* 100 kJ mol^{-1} or higher. When the donor groups and also the acceptor groups are different ($A^1 \neq A^2$, $D^1 \neq D^2$), the twisted molecules are chiral, and two such compounds (**3**), (**4**) have been resolved by low-pressure liquid chromatography on swollen microcrystalline triacetylcellulose.[5]

In this investigation we have chosen to study chiral and achiral push–pull ethylenes with thiocarbonyl groups as electron acceptors. Our motives are an interest in the u.v.–visible absorption spectra of these compounds, which simulate mono- and dithio-1,3-diketone anions, and a wish to explore the different steric and electronic effects of carbonyl and thiocarbonyl groups on the rate of racemization of compounds of this type. The c.d. spectra of the resolved compounds might display transitions which are hidden under stronger bands in the u.v. spectra. Compounds (**5**)—(**10**) were prepared for this study.



(**1**)

Experimental

Preparations.—*1-Benzyl-3-isopropyl-2-(2-oxo-4-thioxopentan-3-ylidene)hexahydropyrimidine* (**5**) *and its Dithione Analogue* (**6**).—The 2-(2,4-dioxopentan-3-ylidene) analogue[6] was treated with one equiv. 2,4-bis-(4-phenoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide[7] in 1,2-dimethoxyethane at 40 °C for 3 h under nitrogen. After evaporation, the crude product was subjected to flash chromatography on silica with toluene–light petroleum as eluant to give first a fraction of red crystalline material (**6**), m.p. 187—188 °C, 13% yield after recrystallization from toluene–light petroleum, and then a fraction of yellow crystals (**5**), m.p. 123—125 °C, 20% yield after recrystallization from toluene–light petroleum: (**5**), *m/z* (70 eV) 330 (*M*, 10%), 297 (34), 287 (10), 254 (20), 212 (12), 98 (13), 91 (90), 65 (25), 56 (29), 43 (100), and 41 (90); (**6**), *m/z* (70 eV) 346 (*M*, 20%), 313 (17), 282 (7), 255 (12), 98 (15), 91 (90), 65 (27), 59 (40), 43 (70), and 41 (100).

1-Benzyl-3-isopropyl-2-(1-phenyl-1-oxo-3-thioxobutan-2-ylidene)hexahydropyrimidine (**7**) *and its Dithione Analogue* (**8**).—These were prepared by thiation of the analogous dione. The starting material for the dione is 1,1-bismethythio-2-acetyl-2-benzoylethylene, the preparation of which in 13% yield has previously been described.[8] By use of dry DMF only as solvent in the reaction, the yield could be increased to 34%.

The preparation of (**7**) and (**8**) was performed as with (**5**) and (**6**). Use of bis-(4-phenoxyphenyl)dithiadiphosphetane disulphide[7] gave the best yield of (**7**) (10 h in dry toluene; room temperature; 22% yield of orange prisms; m.p. 141—145 °C). The best yield of (**8**) was obtained by use of 2,4-bis-(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulphide, the Lawesson reagent,[9] (16 h) in 1,2-dimethoxyethane; room temperature; 13% yield of red prisms; m.p. 153—154 °C): (**7**), *m/z* (70 eV) 392 (*M*, 8%), 359 (35), 255 (55), 212 (8), 105 (25), 98 (13), 91 (100), 77 (35), 65 (15), 56 (20), 45 (35), and 41 (60); (**8**), *m/z* (70 eV) 408 (*M*, 16%), 375 (6), 344 (10), 317 (15), 121 (18), 98 (20), 91 (100), 65 (20), 58 (45), 43 (42), and 41 (90).

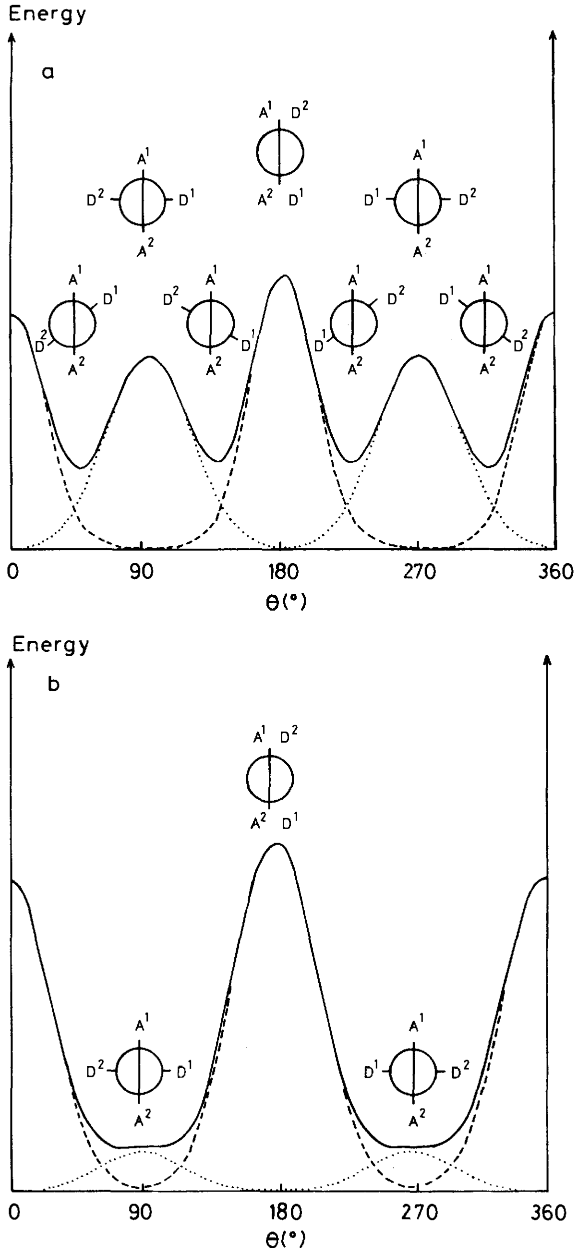
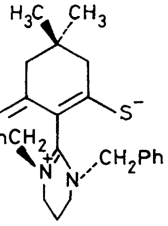
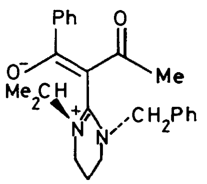


Figure. Potential energy curves for the rotation about the C=C bond in (1). Steric component (– – – –), π-electronic component (· · · ·), total energy (——). θ is the A^1-C=C-D^1 dihedral angle



(2)



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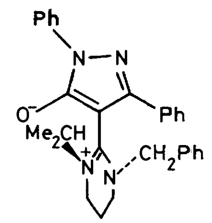

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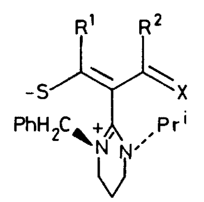
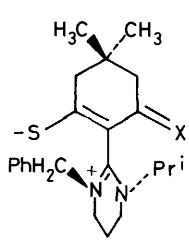
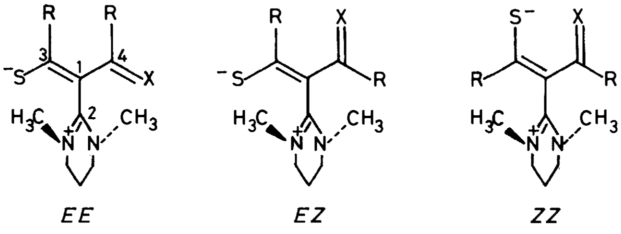


(**5**) R^1 = R^2 = CH$_3$, X = O
(**6**) R^1 = R^2 = CH$_3$, X = S
(**7**) R^1 = CH$_3$, R^2 = Ph, X = O
(**8**) R^1 = CH$_3$, R^2 = Ph, X = S



(**9**) X = O
(**10**) X = S



(**11**)

a; R = CH$_3$, X = O
b; R = CH$_3$, X = S
c; R = H , X = S

1-*Benzyl-3-isopropyl-2-(4,4-dimethyl-2-oxo-6-thioxocyclohexylidene)hexahydropyrimidine* (**9**) *and its 2,6-Bisthioxo Analogue* (**10**).—These were prepared in analogy with the previous compounds, starting from the 2,6-dioxo analogue. The best yield was obtained with the Lawesson reagent[9] [toluene; room temperature; 21 h; 18% yield of (**9**) as yellow prisms, m.p. 198—200 °C and 78% yield of (**10**) as red prisms, m.p. 210—214 °C]: (**9**), m/z (70 eV) 370 (M, 8%), 337 (60), 295 (15), 146 (10), 98 (18), 91 (95), 70 (35), 65 (24), 43 (40), 42 (40), and 41 (100); (**10**), m/z (70 eV) 386 (M, 10%), 353 (50), 311 (10), 295 (8), 146 (10), 98 (20), 91 (98), 70 (45), 65 (23), 56 (30), 43 (60), and 41 (100).

The purity of the compounds was assessed by t.l.c. analysis and by the ^{1}H n.m.r. spectra. All compounds (**5**)—(**10**), and in particular the dithio compounds (**6**), (**8**), and (**10**), are light sensitive.

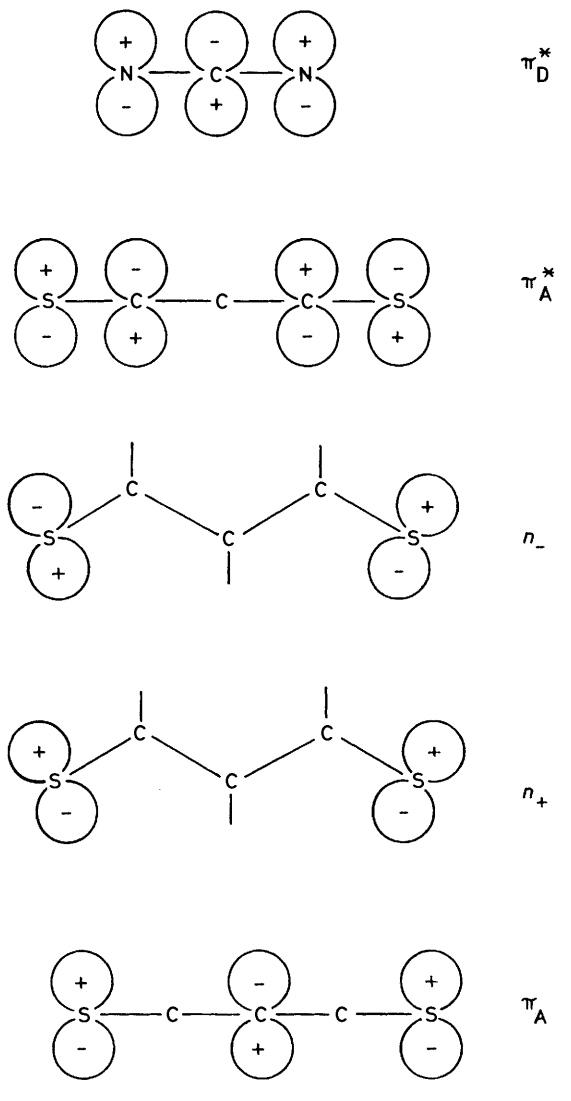
^{1}H N.m.r. (Table 1) were recorded with a Varian XL-300 spectrometer.

The preparative resolution of enantiomers was performed by liquid chromatography on swollen microcrystalline triacetylcellulose (TAC) according to Hesse and Hagel[10] and Mannschreck *et al.*[11] The instrumentation is described by Isaksson and Rochester.[12] All compounds (*ca.* 5 mg quantities) were dissolved in ethanol, the eluant, before injection on the column. Even if the resolution after the first cycle was moderate, virtually complete separation was achieved after three cycles. The optical purity was in all cases ascertained by analysis of the chromatograms, plots of the rotation *versus* the absorbance values giving straight lines.[13] For (**7**) and (**8**), partial resolution of larger quantities (*ca.* 40 mg) was performed, the products were isolated, and their optical purities were assessed by the n.m.r. method, using the 'Pirkle alcohol', (+)-1-(9-anthryl)-2,2,2-trifluoroethanol,[14] before recording their c.d. spectra.

C.d. spectra were recorded with a JASCO J-500A spectropolarimeter, using the ethanol solution containing the enantiomerically pure fraction directly from the TAC column. The concentrations were determined from the u.v. spectra of the solutions. Since the c.d. spectra were weak (Table 4), accumulation of 10—16 spectra was employed to obtain sufficient signal-to-noise ratio. The baselines were recorded in the same way with solutions containing the appropriate

Table 1. ^{1}H N.m.r. spectra [δ (J/Hz); $CDCl_3$; ambient temperature; 300 MHz]

Compound	$(CH_3)_2CH$	5-CH_2	4(6)-CH_2	$(CH_3)_2CH$	$PhCH_2$	CH_3CO	CH_3CS	CH_2CO	CH_2CS	$(CH_3)_2C$	C_6H_5
(5)	1.140 (6.8)	2.086 (m)	3.200 (m)	4.334 (6.8)	4.428 (14.7)	2.304	2.886				7.27—7.35 (5 H)
	1.333 (6.6)		3.343 (m)		4.840						
(6)	1.251 (6.7)	2.024 (quint)	3.055 (t)	4.172 (6.7)	4.549 (s)		2.995				7.28—7.34 (3 H)
			3.278 (m)								7.42—7.47 (2 H)
(7)	1.203 (6.8)	2.08 (m)	3.232 (m)	4.601 (6.6)	4.563 (14.9)		2.222				7.26—7.42 (10 H)
	1.394 (6.6)		3.398 (m)		5.038						
(8)	1.303 (6.6)	2.075 (m)	3.107 (m)	4.465 (6.7)	4.705 (14.4)		2.182				7.27—7.34 (8 H)
	1.315 (6.8)		3.339 (m)		4.757						7.48—7.51 (2 H)
(9)	1.166 (6.8)	2.041 (m)	3.206 (m)	4.271 (6.6)	4.424 (14.9)			2.223	2.768 (16.8)	0.994 (s)	7.27—7.36 (5 H)
	1.319 (6.6)		3.372 (m)		4.754				2.804	1.055 (s)	
(10)	1.253 (6.7)	2.059 (quint)	3.112 (t)	4.152 (6.7)	4.527 (s)				2.766 (16.9)	1.014 (s)	7.27—7.36 (3 H)
			3.339 (m)						2.814	1.039 (s)	7.43—7.49 (2 H)



Scheme.

concentrations of racemic material in order to perform the measurements on solutions with the same optical densities. The spectra reported in Table 4 are for the E_1 enantiomers. The spectra for the E_2 enantiomers appear as mirror images.

The kinetic study of the racemization of (**5**) and (**7**)—(**9**) was performed by heating ethanolic solutions of the pure enantiomers in sealed glass ampoules in a thermostatted paraffin oil-bath for suitable times, covering 2—3 half-lives. The degree of racemization was monitored by recording the c.d. absorption of the long-wavelength band in a 1.0 cm cell. The racemization was found to follow first-order kinetics, but the u.v. spectra of the heated solutions showed that a thermal decomposition also took place, eventually leading to the appearance of a new band at shorter wavelength than the strong long-wavelength band. The loss of intensity of the latter band was taken as a measure for the decomposition and used to correct the rate of racemization. For (**5**), (**7**), and (**8**), this was a minor correction, but for (**9**) the rates of racemization and decomposition were nearly the same, and the barrier obtained for this compound is therefore a lower limit to the true barrier to rotation. The kinetic data and the barriers are found in Table 2. In principle, it is preferable to study the kinetics by monitoring the c.d. spectra rather than the optical rotation, since the former are more sensitive and also indicate if new optically active compounds should be formed.

U.v.–visible spectra (Table 3) were recorded with a Cary model 219 spectrophotometer.

CNDO/S Calculations were performed as described in ref. 4, using an idealized geometry with a 90° C(3)C(1)C(2)N dihedral angle and a C(1)–C(2) bond length of 1.482 Å as for (**2**). Calculations were performed for the *EE*, *EZ*, and *ZZ* conformations.

Results and Discussion

The permanently twisted character of (**5**) and (**7**)—(**10**) follows from the ^{1}H n.m.r. spectra (Table 1). The *N*-benzylmethylene proton resonances of (**5**) and (**7**)—(**9**) appear as AB systems, and the isopropyl methyl resonances as doublets of doublets, reflecting two different acceptor groups in a twisted system. Similarly, the ring methyl and methylene resonances in (**9**) and (**10**) appear as doublets and AB systems respectively, in response to the different *N*-substituents in the donor part. Only (**6**) lacks prochiral groups to demonstrate the twist.

The assignment of the benzoyl-thioacetyl rather than the thiobenzoyl-acetyl structure to (**7**) is based on the similarity of the ^{1}H chemical shifts of the acceptor methyl protons in (**7**) and (**8**) and also on the appearance of a peak at m/z 105, corresponding to the benzoyl ion, in the mass spectrum of (**7**). This peak is absent in the spectrum of (**8**), which instead has a peak at m/z 121, corresponding to the thiobenzoyl ion.

The room-temperature n.m.r. spectra show no selective broadening which could indicate rate constants $> 1\ s^{-1}$ ($\Delta G^\ddagger >$ 70 kJ mol^{-1}) for passage through the planar state with concomitant exchange of diastereotopic protons. Instead, the resolution and controlled racemization of the chiral compounds (**5**) and (**7**)—(**9**) shows that the free energy barriers for this

Table 2. Kinetic data and free energy barriers for rotation through the planar state (solvent EtOH)

Compound	Temperature (°C)	$\tau_{\frac{1}{2}}$(rac)/h	$\Delta G^{\ddagger}_{rot}$/kJ mol^{-1}
(6)	91	20.0	126.8 ± 0.2
(7)	90	22.2	126.8 ± 0.2
(8)	90	13.0	125.1 ± 0.3
(9)	90	>24.5	>127

Table 3. U.v.–visible absorption spectra

Compound	Solvent	Experimental	Calculated (*EE*)		
		$\lambda_{max.}$/nm(ε)	$\lambda_{max.}$/nm	f[a]	Assignment[b]
(5)	EtOH	355 (22 500)			
		223 (19 000)			
	CH_2Cl_2–C_6H_{12} (1:9)	419s (390)	418.7	0.0000	$n_s \longrightarrow \pi^*_A$
		359 (25 000)	290.6	0.1982	$\pi_A \longrightarrow \pi^*_A$
		294 (4 900)	256.7	0.0331	$n_s \longrightarrow \pi^*_D$
		225 (19 000)	223.7	0.1139	$n_o \longrightarrow \pi^*_D$
(6)	EtOH	434 (28 000)			
		224 (17 500)			
	CH_2Cl_2–C_6H_{12} (1:9)	548 (330)	512.1	0.0000	$n_- \longrightarrow \pi^*_A$
		520 (360)	486.2	0.0000	$n_+ \longrightarrow \pi^*_A$
		437 (30 000)	397.5	0.2683	$\pi_A \longrightarrow \pi^*_A$
		300s (4 000)	305.3	0.0319	$n_- \longrightarrow \pi^*_D$
		226 (16 000)	270.4	0.2031	$n_+ \longrightarrow \pi^*_D$
(7)	EtOH	336 (21 000)			
		225 (20 000)			
	CH_2Cl_2–C_6H_{12} (1:9)	370 (19 000)			$\pi_A \longrightarrow \pi^*_A$
		294 (4 500)			
		229 (21 000)			
(8)	EtOH	442 (28 300)			
		300 (500)			
		227 (18 800)			
	CH_2Cl_2–C_6H_{12} (1:9)	567 (550)			$n_- \longrightarrow \pi^*_A$
		445 (31 500)			$\pi_A \longrightarrow \pi^*_A$
		307 (7 000)			
		231 (17 500)			
(9)	EtOH	345 (27 000)			
		222 (19 000)			
	CH_2Cl_2–C_6H_{12} (1:9)	419 (357)			
		348 (27 500)	As for **(5)**		
		304 (4 000)			
		228 (20 000)			
(10)	EtOH	420 (51 000)			
		225 (20 000)			
	CH_2Cl_2–C_6H_{12} (1:9)	510 (280)	As for **(6)**		
		422 (59 000)			
		284 (5 000)			
		228 (21 000)			

[a] Oscillator strength. [b] Dominating configuration from CI calculation.

process are 125—>127 kJ mol^{-1}. These barriers are thus considerably higher than the 107 kJ mol^{-1} found for the dicarbonyl analogue of **(7)** and **(8)**.[5] To explain this difference, we have to consider both steric and electronic factors. Low-temperature ^{1}H n.m.r. studies of analogues of **(6)** and **(8)** show no splitting of the thioacetyl resonances, indicating one preferred conformation, symmetrical for **(6)** and most likely *EE*.[15] In the 1,1-diacetyl analogues, the *EE* and *EZ* forms were observed, whereas the *ZZ* form was only demonstrated as a high-energy intermediate in the *EZ* $\rightleftharpoons$ *ZE* exchange.[6] In the thio analogues, the *ZZ* form should be even more destabilized by steric repulsion. It is worth noting that Raban and Shmyr[16] have recently shown that the thioacetyl group in *N*-acetylthioacetamide, which has some structural similarity to the acceptor part of **(5)**, only takes up the *E* conformation in the absence of potassium ions. The *EE* conformations for **(5)** and **(6)** are strongly supported by the similarities of the chemical shifts for the Pr^i and $PhCH_2$ protons in **(5)** and **(9)** and in **(6)** and **(10)**, indicating that these protons have rather similar environments in the respective pairs of compounds. The larger bulk of the sulphur atoms therefore leads to a stronger congestion of the transition state. It can be assumed that the (thio)acyl groups in **(5)**—**(8)** are rotated out of the plane of the acceptor groups [the C(3)C(1)C(4) plane] to minimize the steric interaction in the transition state, and therefore the 'stiffness' of the acceptor part will play a role.

The electronic effects on the barriers can be described as ground-state and transition-state stabilizations due to delocalization effects, and as transition-state destabilization due to stiffening of the acceptor part. All three effects are stronger in thiocarbonyl than in carbonyl compounds,[17,18] being of the type $X{=}C{-}C{=}C{-}Y^- \longleftrightarrow {}^-X{-}C{=}C{-}C{=}Y$ (X/Y = O/O,O/S, or S/S) in the ground state and $X{=}C{-}C{=}C{-}NR_2 \longleftrightarrow {}^-X{-}C{=}C{-}C{=}{}^+NR_2$ (X = O or S) in the transition state. It is not possible to determine the exact balance between these effects, since the magnitude of the purely steric effect is unknown, but the high barriers make it likely that the ground-state stabilization and the stiffening of the transition state dominate.

The u.v.–visible absorption spectrum of the dithio compound **(10)** (Table 3) is quite similar to that of the analogue **(2)** with a five-membered donor ring described in ref. 4. A significant difference is that the two strong bands at 422 (shoulder) and 417.5 nm for **(2)** are replaced by one symmetrical band at 422 nm (solvent cyclohexane–methylene dichloride 9:1). The splitting of the band for **(2)** was tentatively described as vibrational fine structure. This band can profitably be compared with the strong band at 414 nm reported for the anion of 3-methylpentane-2,4-dithione.[19] A difference is also found for the second strong band, which appears at 228 nm for **(10)** and at 235 nm for **(2)**. The transition energies and oscillator strengths calculated for **(10)** agree reasonably well with the experimental values. However, while the agreement for the first strong $\pi \longrightarrow \pi^*$ band is better for **(10)** than for **(2)**, that for the second strong band, ascribed to an $n_+ \longrightarrow \pi^*_D$ charge-transfer transition, n_+ being the symmetric combination of the thiocarbonyl lone pair orbitals and π^*_D the orbital in the donor part (π^*_D, Scheme), has become worse. The calculations predict a red shift from **(2)** to **(10)**, in agreement with the improved overlap between the n_+ and π^*_D orbitals, but the experimental result is a blue shift. The bisthioacetyl compound **(6)**, which has a chromophoric system similar to that of **(10)**, shows red shifts of all bands except that for $n_+ \longrightarrow \pi^*_D$ at 226 nm, and it shows two weak long-wavelength bands at 548 and 520 nm ascribed to $n_- \longrightarrow \pi^*_A$ and $n_+ \longrightarrow \pi^*_A$ transitions and predicted by calculations, n_- being the antisymmetric combination of the C=S lone pair orbitals and π^*_A the LUMO in the $S{=}C{-}C{=}C{-}S^-$ part. When CNDO/S calculations are performed for the *EZ* and *ZZ* forms, the agreement is much worse, especially for the $n_- \longrightarrow \pi^*_A$ transitions, which are predicted at unreasonably long wavelengths. This could be due to too close S/CH_3 and S/S contacts, but even with 1,1-bisthioformyl-2,2-diaminoethylene **(11c)**, the $n_- \longrightarrow \pi^*_A$ transitions are predicted at 567, 693, and 1 777 nm for the *EE*, *EZ*, and *ZZ* forms, respectively. This is a further argument for the dominance of the *EE* form in **(6)**.

The 1-thioacetyl-1-thiobenzoyl analogue **(8)** has a rather similar spectrum, with moderate bathochromic shifts of all bands due to conjugation with the benzene ring. Only one isolated $n \longrightarrow \pi^*_A$ band is observed.

The spectra of the 1-acyl-1-thioacyl compounds are of the same general type as those of the dithio analogies, although all bands appear at appreciably shorter wavelengths, only the second strong band ($n \longrightarrow \pi^*_D$) being less strongly

Table 4. Circular dichroism spectra of the E^1 enantiomers in ethanol

Compound	λ/nm	Δε	λ/nm	Δε	λ/nm	Δε
(5)	390	+0.35	303	+0.25	238	−0.70
(7)	413	+2.56			232	−7.66
(8)	563	+1.55	453	−0.53	307	−1.09
(9)	378	+3.00	295	+1.50	235	−14.2

shifted. The $n_s \longrightarrow \pi_A^*$ bands are shifted by 90—130 nm, and in the benzoyl compound (**7**) this band is not visible, being hidden under the strong band at 370 nm. It is interesting to compare the $\pi_A \longrightarrow \pi_A^*$ band for (**5**), 355 nm (22 500) in ethanol, with the strong band at 352 nm reported by Fabian[20] for the anion of monothioacetylacetone, which should have the same origin.

When the solvent is changed to ethanol, all $n \longrightarrow \pi_A^*$ bands undergo hypsochromic shifts to the extent that they become hidden under the nearby strong bands ($\pi_A \longrightarrow \pi_A^*$). These are also shifted, but only 2—4 nm to shorter wavelengths. The solvent effect on the $n \longrightarrow \pi_A^*$ bands is diagnostic for this kind of transition.

The c.d. spectra (Table 4) are quite weak. It is noteworthy that the transitions, which give rise to the first strong $\pi \longrightarrow \pi^*$ bands in the u.v. spectra, give no distinct c.d. bands. The long-wavelength c.d. bands for all compounds are most likely due to $n_s \longrightarrow \pi_A^*$ transitions, and the bands at 563 and 543 nm for (**8**) are ascribed to the $n_- \longrightarrow \pi_A^*$ and $n_+ \longrightarrow \pi_A^*$ transitions. The bands at 232—238 nm are probably due to $n \longrightarrow \pi_D^*$-type transitions, shifted to longer wavelengths by overlap with a positive band at shorter wavelength. No similar band is seen for (**8**), possibly due to complete elimination through the positive band. Owing to strong u.v. absorption and weak c.d. effect, the measurement in this region is uncertain.

The absence of bands corresponding to the $\pi_A \longrightarrow \pi_A^*$ transitions may be due to twist angles close to 90°, which would minimize the coupling between this and the $\pi_D \longrightarrow \pi_D^*$ transition. The rotational strengths of the $n \longrightarrow \pi^*$ transitions are due to the difference in chiral perturbation by the *N*-benzyl and *N*-isopropyl groups.

Acknowledgements

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