Rotational isomerism and crystal structures of 2,2′-diphenyl-2,2′-bi-1,3-dithianyl and 2,2′-diphenyl-2,2′-bi-1,3-dioxolanyl †

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Dipole moments of the compounds 2,2′-diphenyl-2,2′-bi-1,3-dithianyl **1** and 2,2′-diphenyl-2,2′-bi-1,3-dioxolanyl **2** in carbon tetrachloride and benzene have been measured over a range of temperatures. The crystal and molecular structures of the compounds were determined by single-crystal X-ray diffraction methods. Analyses of the crystal structures and relative permittivity data show that the compounds exist in the *trans* conformation in the solid state and as rotameric mixtures in solution with a predominantly high *trans* population of 85% and 80% respectively at 25 °C. The experimentally derived values of the energy difference between the *gauche* and *trans* rotamers and the *gauche/trans* population quotients were compared with the values predicted by molecular orbital calculations.

Introduction

Our interest in the rotational isomerism of substituted ethanes has led us to investigate the influence of heterocyclic groups in such molecules. Earlier studies[1–4] on 1,3-dithianes and 1,3-dioxolanes have shown that these compounds differ from their cycloalkane analogues and their conformational effects are not explained by steric and dipolar interactions alone. Although many physical studies on the 1,3-dithiane and 1,3-dioxolane series have been made, only a few studies have been reported on the bi-1,3-dioxolanyl series[5–7] and, to our knowledge, there have been no reports on the bi-1,3-dithianyl molecules. We now report our findings on 2,2′-diphenyl-2,2′-bi-1,3-dithianyl **1** and 2,2′-diphenyl-2,2′-bi-1,3-dioxolanyl **2**, based on X-ray diffraction measurements, dipole moment determination and molecular orbital calculations. These results are compared with compounds in the 1,1′-diphenyl-1,1′-bicycloalkyl series[8] which generally prefer the *trans* conformation, except for 1,1′-diphenyl-1,1′-bicyclopentyl where the molecules exist predominantly in the *gauche* form.

Experimental

Preparation of compounds

Compounds **1** and **2** were synthesised by free-radical dimerisation with *tert*-butyl peroxide.[9] Materials for the synthesis were from commercial sources and used without further purification. Analytical thin-layer chromatography was performed on EM Reagent 0.25 silica gel 60-F plates. Flash chromatography was performed using EM silica gel 60 (230–400 mesh). To our knowledge compounds **1** and **2** have not been reported previously.

2,2′-Diphenyl-2,2′-bi-1,3-dithianyl 1. To 2-phenyl-1,3-dithiane (2.95 g, 15.0 mmol) was added *tert*-butyl peroxide (1.30 g, 8.9 mmol) and the reaction was gently refluxed under nitrogen for 3 days. The brownish solution obtained was concentrated, diluted with ether, washed with water and purified by flash chromatography (hexane–chloroform 1:3, R_f = 0.53) to give 2,2′-diphenyl-2,2′-bi-1,3-dithianyl **1** as a white solid (2.46 g, 42%): mp 205.0 °C (from chloroform) [Found: C, 61.31; H, 5.30; S, 32.93%; M⁺, 390. $C_{20}H_{22}S_4$ requires C, 61.49; H, 5.67; S, 32.83%; M, 390]. δ_H (300 MHz; CDCl₃; Me₄Si) 1.7–2.0 (4H, m, CH₂C*H₂*CH₂), 2.5–2.7 (8H, m, SC*H₂*CH₂C*H₂*S), 7.1–7.2 (6H, m *meta*-H and *para*-H) and 7.5 (4H, d, *ortho*-H).

2,2′-Diphenyl-2,2′-bi-1,3-dioxolanyl 2. The procedure for the preparation of **1** was used. 2-Phenyl-1,3-dioxolane (2.25 g, 15 mmol) on reaction with *tert*-butyl peroxide (1.30 g, 8.9 mmol) gave 2,2′-diphenyl-2,2′-bi-1,3-dioxolanyl **2** as a white solid (2.32 g, 52%) after purification by chromatography (hexane–ethyl acetate 3:1, R_f = 0.60): mp 230.0 °C (from hexane) [Found: C, 72.44; H, 5.97%; M⁺, 298. $C_{18}H_{18}O_4$ requires C, 72.46; H, 6.08%; M, 298]. δ_H (300 MHz; CDCl₃; Me₄Si) 3.8 (8H, s, C*H₂*CH₂) and 7.4–7.2 (10H, m, Ph).

Crystal structure determination and refinement

Single crystals of **1** were obtained from hexane and **2** from chloroform.

Crystal data of **1**: $C_{20}H_{22}S_4$, M = 390.62. Monoclinic, colourless blocks, a = 15.489(3) Å, b = 7.787(1) Å, c = 15.793(3) Å, β = 101.341(1)°, V = 1867.84(6) Å³, space group $P2_1/c$, Z = 4, D_x = 1.389 g cm⁻³. Crystal dimension: 0.33 × 0.25 × 0.23, μ(Mo-Kα) = 0.508 mm⁻¹, 11341 reflections measured, 4566 unique (R_{int} = 0.0227) which were used in all calculations. The final R and R_w were 4.84% and 10.79% (for $I > 2\sigma(I)$). Crystal data of **2**: $C_{18}H_{18}O_4$, M = 298.3. Monoclinic, colourless prisms, a = 6.059(3) Å, b = 6.944(4) Å, c = 17.666(1) Å, β = 94.023(1)°, V = 741.50(7) Å³, space group $P2_1/n$, Z = 2, D_x = 1.336 g cm⁻³. Crystal dimension: 0.40 × 0.37 × 0.15, μ(Mo-Kα) = 0.094 mm⁻¹, 4412 reflections measured, 1789 unique (R_{int} = 0.0167) which were used in all calculations. The final R and R_w were 3.89% and 9.56% (for $I > 2\sigma(I)$).

Intensity data were collected at room temperature using a Siemens R3m/V diffractometer with Mo-Kα radiation (λ = 0.71060 Å). Lorentz and polarisation corrections, structure solution by direct methods, full-matrix least-squares refinements and preparation of figures were all performed by the SHELXTL-Plus PC program package.[10] All non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were placed at calculated positions with the isotropic displace-

ment coefficient being assigned a value that is 1.6 times that of the atom to which it is attached. CCDC reference number 188/267. See http://www.rsc.org/suppdata/p2/b0/b003961f for crystallographic files in .cif format.

Dipole moment determination

Relative permittivities were determined with a heterodyne-beat meter [11] and densities and refractive indices by standard procedures.[12] All solvents were carefully distilled and dried before use. The physical constants required for the relative permittivity have been given previously.[13,14]

Molecular orbital calculations

Standard *ab initio* and density functional calculations were carried out using the GAUSSIAN 98 series of programs.[15] Geometry optimisations were performed at the B3-LYP[16] level using the split-valence polarised 6-31G* basis set.[17] Harmonic vibrational frequencies were computed at the B3-LYP/6-31G* level in order to characterise the stationary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to evaluate zero-point energies (ZPEs), scaled by a factor of 0.9804.[18] Unless otherwise noted, all relative energies reported in the text correspond to the B3-LYP/6-311+G(2d,p) values and all structural parameters correspond to the B3-LYP/6-31G* values.

Results and discussion

Selected bond lengths, bond angles and torsion angles of **1** and **2** are given in Tables 1 and 3.

X-Ray structure determination of 2,2′-diphenyl-2,2′-bi-1,3-dithianyl 1

Each asymmetric unit of the cell contains two independent molecules in general positions. Although the molecule does not have crystallographic symmetry, it shows approximate two-fold rotational symmetry. Fig. 1 depicts the structure and defines the atomic numbering of the molecules. The independent molecules are essentially identical structures. Equivalent bond lengths and bond angles differed by less than 0.02 Å and 1° respectively.

Molecule **1** exists in the *trans* conformation in the solid state with the dithiane rings adopting the chair form. Assuming that the chair form is the favoured ring geometry, two conformations may occur with regard to the position of the *exo* (C(1)–C(1A)) bond: pseudoequatorial (e) or pseudoaxial (a). Ring inversion leads to three possible combinations of the two dithiane rings: ee, ea and aa (Fig. 2). The resulting X-ray crystal structure of **1** shows that in the solid-state, only the *trans*-ee conformation is realised. Each dithiane ring has an approximate mirror plane and the phenyl groups are placed perpendicular to the planes. Although the same conformation has been observed in 1,1′-diphenyl-1,1′-bicyclohexyl,[19] these results contrast with 2-phenyl-1,3-dithiane[20] and other 2-aryl substituted 1,3-dithianes[21] where the aryl groups have been shown to favour the equatorial position. This difference in conformational behaviour may be partly attributed to the salient interaction between the vicinal phenyl ring and the *syn*-axial hydrogens in the ea and aa configurations, thus making these conformations prohibitive and forcing the molecule into the ee arrangement. The ee configuration is further stabilised by the anomeric effect caused by the hyperconjugative interaction between the lone pairs on the endocyclic sulfur and the antibonding σ*-orbital of the aryl–C-2 bond. Since the interacting orbitals overlap effectively only in the axially substituted isomer (Fig. 2), this implies that only these species are stabilised by this interaction, thus lending further support to the preference of the ee configuration.
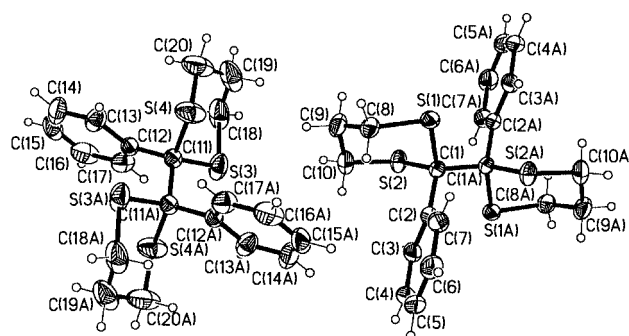

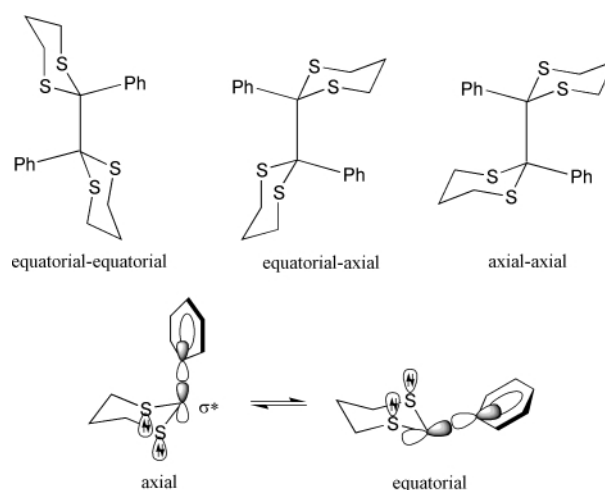**Fig. 1** Thermal ellipsoid diagram of **1**.

Fig. 2 Possible *trans* conformers of **1**.

The central C–C bond in **1** (1.592(4) Å) is shorter than in 1,1′-diphenyl-1,1′-bicyclohexyl (1.627(5) Å). This can be explained by (i) the longer C–S bond which lowers the degree of interaction between the phenyl and dithiane moieties and (ii) the replacement of the CH₂-groups at the C-2 and C-6 positions of the cyclohexane chair by bare sulfur atoms whose smaller van der Waals radius reduces the steric repulsion caused by the compression of the *ortho*-hydrogens of the phenyl rings with the equatorial hydrogens at C-2 and C-6 of the cyclohexyl rings. In contrast to 1,1′-diphenyl-1,1′-bicyclohexyl, the C–C–C and C–C–S angles in **1** are widened in preference to the C–S–C angles. This opening up of the C–C–C and C–C–S angles compensates for the puckering effect of the small C–S–C angles so that the dihedral angles in the dithiane ring is larger than the 56° commonly accepted for cyclohexane.[22] In the crystal of **1**, the dihedral angles of the dithiane rings are 63.1 ± 2.5°.

Dipole moment measurements of 1

The results of the dipole moment measurements of **1** are presented in Table 2 with standard notation. Three concentration dependencies, namely those of the relative permittivities, densities and refractive indices ($a\varepsilon_1$, βd_1 and γd_{12}) were determined for each solvent at the three temperatures. Using the least squares method, the experimental values of the slopes $a\varepsilon_1$, βd_1 and $\gamma n_1{}^2$ (given by eqn. (1)) at infinite dilutions of

$$a\varepsilon_1 = \left(\frac{\delta\Delta\varepsilon}{\delta w_2}\right)_{w_2 \longrightarrow 0} \qquad \beta d_1 = \left(\frac{\delta\Delta d}{\delta w_2}\right)_{w_2 \longrightarrow 0}$$

$$\gamma n_1{}^2 = \left(\frac{\delta\Delta n^2}{\delta w_2}\right)_{w_2 \longrightarrow 0} \qquad (1)$$

the compounds (w_2 denoting the solute weight fraction) and the respective molar polarisation, refractions and dipole moments

Table 1 Selected bond lengths (Å), bond angles and torsion angles (°) of **1**

S(1)–C(8)	1.811(2)	S(1)–C(1)	1.842(2)
S(2)–C(10)	1.817(2)	S(2)–C(1)	1.851(2)
C(1)–C(2)	1.538(3)	C(1)–C(1A)	1.592(4)
C(8)–C(9)	1.512(4)	C(9)–C(10)	1.525(4)
S(3)–C(18)	1.804(3)	S(3)–C(11)	1.846(2)
S(4)–C(20)	1.829(3)	S(4)–C(11)	1.834(2)
C(11)–C(12)	1.538(3)	C(11)–C(11A)	1.593(4)
C(18)–C(19)	1.490(6)	C(19)–C(20)	1.520(6)
C(8)–S(1)–C(1)	100.5(1)	C(10)–S(2)–C(1)	100.0(1)
C(2)–C(1)–C(1A)	112.6(2)	C(2)–C(1)–S(1)	111.7(1)
C(1A)–C(1)–S(1)	106.3(2)	C(2)–C(1)–S(2)	111.3(1)
S(1)–C(1)–S(2)	107.6(1)	C(3)–C(2)–C(7)	117.7(2)
C(9)–C(8)–S(1)	113.8(2)	C(8)–C(9)–C(10)	113.2(2)
C(9)–C(10)–S(2)	114.8(2)	C(17)–C(12)–C(13)	117.4(2)
C(8)–S(1)–C(1)–C(2)	−59.26(16)	C(8)–C(9)–C(10)–S(2)	−63.66(26)
C(8)–S(1)–C(1)–S(2)	63.25(12)	C(10)–S(2)–C(1)–C(2)	60.67(16)
C(10)–S(2)–C(1)–S(1)	−62.04(13)	C(1A)–C(1)–C(2)–C(3)	−89.31(26)
S(1)–C(1)–C(2)–C(3)	151.19(17)	C(1)–S(1)–C(8)–C(9)	−62.81(19)
C(20)–S(4)–C(11)–C(12)	−61.51(21)	C(20)–S(4)–C(11)–C(11A)	175.05(23)
C(20)–S(4)–C(11)–S(3)	60.80(18)	C(18)–S(3)–C(11)–S(4)	−62.46(16)
C(18)–C(19)–C(20)–S(4)	62.80(35)	C(11)–S(3)–C(18)–C(19)	63.31(28)
C(11A)–C(11)–C(12)–C(17)	−88.97(29)	S(1)–C(8)–C(9)–C(10)	64.25(26)
S(3)–C(18)–C(19)–C(20)	−65.05(35)		

Table 2 Molar polarisation, refractions and dipole moments at infinite dilution of 2,2′-diphenyl-2,2′-bi-1,3-dithianyl **1** and 2,2′-diphenyl-2,2′-bi-1,3-dioxolanyl **2**

$T/°C$	Solvent	Conc. range $(10^5 w_2)$	$a\varepsilon_1$	β	γ	P_2/cm^3	R_D/cm^3	$\mu^a/10^{30}$ C m
2,2′-Diphenyl-2,2′-bi-1,3-dithianyl **1** ($R_D = 115.62$ cal)								
7	CCl$_4$	120–280	2.88	−0.147		196.6		6.20 ± 0.02
25	CCl$_4$	130–240	2.53	−0.411	0.129	205.8	114.86	6.78 ± 0.03
45	CCl$_4$	140–230	2.55	−0.374		208.9		7.13 ± 0.04
7	Benzene	290–630	1.29	0.422		167.6		4.86 ± 0.02
25	Benzene	390–600	1.28	0.452	0.148	167.2	116.17	4.99 ± 0.04
45	Benzene	290–610	1.12	0.304		178.5		5.76 ± 0.02
2,2′-Diphenyl-2,2′-bi-1,3-dioxolanyl **2** ($R_D = 81.75$ cal)								
7	CCl$_4$	140–250	2.47	−0.165		138.7		5.20 ± 0.03
25	CCl$_4$	150–270	2.38	−0.200	0.160	140.7	80.20	5.55 ± 0.02
45	CCl$_4$	140–330	1.72	−0.580		143.5		5.79 ± 0.04
7	Benzene	285–630	1.19	0.347		130.3		4.89 ± 0.02
25	Benzene	300–540	1.13	0.269	0.063	137.4	81.48	5.31 ± 0.02
45	Benzene	290–600	1.15	0.288		189.3		5.71 ± 0.03

$^a P_D = 1.05 R_D$.

were calculated. By measuring the relative permittivity effects in extremely dilute solutions of solutes in non-polar solvents like carbon tetrachloride and benzene, we may interpret our present system as consisting of isolated molecules immersed in a well-defined environment. The dipole moments were determined using the method of LeFevre and Vine.[12,23]

Table 2 shows that the dipole moment of the compound increases with increasing temperature in both carbon tetra-chloride and benzene solutions, indicating that the *trans* conformer is more stable than the *gauche*, and is higher in population in these solvents. Application of the Lennard-Jones–Pike method of analysis[24] to our dipole moment data in carbon tetrachloride yields a ΔE (= $E_g − E_t$) value of 6.00 kJ mol^{-1} and a *gauche* conformer dipole moment (μ_g) of 17.28×10^{-30} C m.

Assuming that μ_g is independent of temperature, an estimate of the *gauche*-conformer population ($x\%$) in solution can be made from eqn. (2), which on substituting the observed moment

$$x = \frac{100\mu_{obs}^2}{\mu_g^2} \quad (2)$$

and μ_g values yields a population of 15% *gauche* and 85% *trans* at 25 °C.

The dipole moments of compounds can be understood on the basis of the *trans* ⇌ *gauche* equilibrium; the equilibrium constant is presumably governed by the balance between steric, stereoelectronic and electrostatic factors. In **1**, the *trans* form possesses two synclinal interactions between the C–S–C atoms and the opposite phenyl group whereas the *gauche* form contains only one such interaction. Notwithstanding these steric repulsions, the *trans* conformer is preferred over the *gauche*. The preference of the *trans* conformer could plausibly be attributed to the greater steric strain when the phenyl groups are in the *gauche* position. Since phenyl groups also generally favour the antiparallel configuration,[25] such a conformation, as compared to the *gauche* form, would therefore be the dominant conformer.

For a benzene solution, the Lennard-Jones–Pike analysis gave 7.46 kJ mol^{-1} for ΔE, 17.68×10^{-30} C m for μ_g and 91.9% for the *trans* population.

X-Ray structure determination of 2,2′-diphenyl-2,2′-bi-1,3-dioxolanyl 2

Molecules of **2** lie at general sites but, like in compound **1**, show approximate two-fold symmetry. The molecule as a whole adopts a *trans* conformation, like 2,2′-bi-1,3-dioxolanyl[6]

Table 3 Selected bond lengths (Å), bond angles and torsion angles (°) of **2**

O(1)–C(1)	1.415(2)	O(1)–C(2)	1.437(2)
O(2)–C(1)	1.418(2)	O(2)–C(3)	1.438(2)
C(1)–C(4)	1.532(2)	C(1)–C(1A)	1.549(2)
C(2)–C(3)	1.510(2)		
C(1)–O(1)–C(2)	106.31(10)	C(1)–O(2)–C(3)	104.46(10)
O(1)–C(1)–O(2)	105.58(9)	O(1)–C(1)–C(4)	111.06(9)
O(2)–C(1)–C(4)	111.22(9)	O(1)–C(1)–C(1A)	107.77(11)
O(2)–C(1)–C(1A)	108.01(12)	C(4)–C(1)–C(1A)	112.86(12)
O(1)–C(2)–C(3)	105.14(11)	O(2)–C(3)–C(2)	104.51(11)
C(2)–O(1)–C(1)–O(2)	−32.73(12)	C(2)–O(1)–C(1)–C(4)	87.93(13)
C(1)–O(1)–C(2)–C(3)	14.08(15)	O(1)–C(2)–C(3)–O(2)	9.03(16)
O(1)–C(1)–C(4)–C(5)	30.29(15)	C(3)–O(2)–C(1)–O(1)	38.51(12)
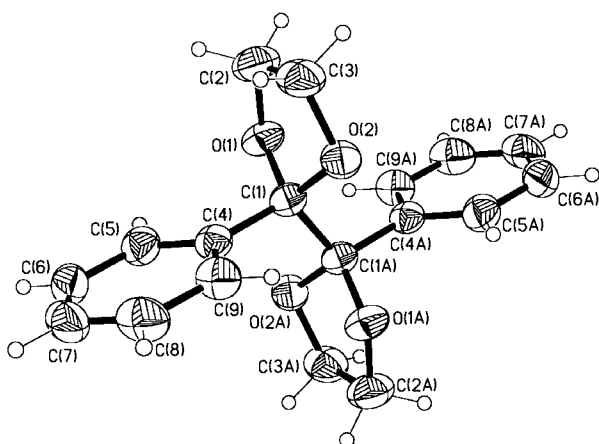
Fig. 3 Thermal ellipsoid diagram of **2**.

and 4,4′,5,5′-tetrachloro-2,2′-bi-1,3-dioxolanyl[7] but unlike its hydrocarbon analogue, 1,1′-diphenyl-1,1′-bicyclopentyl,[19] which has a *gauche* structure with a Ph–C–C–Ph torsion angle of 51.7(4)°. The resulting structure of **2** (Fig. 3) shows that both dioxolane rings are attached by a bond that is equatorial to both rings with C(1A)–C(1)–O(1)–C(2) and C(1A)–C(1)–O(2)–C(3) torsion angles being 147.97(13) and 153.58(12)° respectively. The dioxolane rings show an envelope conformation with O(1), C(2), C(3) and O(2) in a common plane (rms deviation 0.0423 Å) and C(1) 0.4986 Å above it. This conformation differs significantly from 2,2′-bi-1,3-dioxolanyl[6] where the dioxolane ring was shown to be skewed with atoms C(2) and C(3) lying on one side at 0.25 and 0.60 Å from the O(1), C(1) and O(2) plane. The deviation from planarity was attributed to the repulsive forces between the neighbouring methylene groups with the deformation of the five-membered ring providing a more favourable H–H distance (2.4–2.5 Å as compared to 2.25 Å in the planar configuration). In **2**, the H(2) and H(3) atoms are in approximate *cis* positions with a separation of 2.203 Å. These results indicate that though the conformational changes in 1,3-dioxolane are quite facile, external substitutions would introduce an energy barrier in its pseudorotation circuit so that as the substituents become larger or more numerous, their own steric requirements seem to confine the ring to certain definite energy minima, whose position, in the pseudorotation circuit of the ring, is dictated by the steric requirement of the substituent rather than that of the ring.

Dipole moment measurement of 2

Analysis of the data in Table 2 shows that the dipole moments obtained in both solvents increase with increasing temperature, indicating that the *trans* conformer is more stable than the *gauche*, and is higher in population in these solvents. Application of the Lennard-Jones–Pike[24] method of analysis to our

dipole moment data in carbon tetrachloride yields a ΔE value of 5.29 kJ mol^{-1} and a *gauche* conformer dipole moment (μ_g) of 12.54×10^{-30} C m. From eqn. (2), the percentage *trans* population at 25 °C was found to be 80%. These results contrast with bi-1,3-dioxolanyl which exists as a *trans* conformer in the solid-state but favours the *gauche* form when it is in carbon tetrachloride or benzene solutions.[5] This difference in conformation behaviour provides further evidence for the steric hindrance from the phenyl rings.

The experimental data for benzene solutions show that the dipole moment results are very similar to those for carbon tetrachloride solutions. The dipole moment of the *gauche* conformer is however 15.88×10^{-30} C m, which is 3.34×10^{-30} C m higher than that found in carbon tetrachloride. It appears therefore that, unlike **1**, the intermolecular interactions between **2** and the benzene solvent molecules cause an appreciable extent of conformational changes in the molecule. This could be attributed to the greater conformational mobility of the five-membered rings. Conformational analyses of 1,3-dioxolanes[26] have shown that the five-membered ring has a large number of minimum-energy conformations and the free energy differences between these diastereoisomers are small (0.2–1.2 kJ mol^{-1}). The torsional angles of the molecule may therefore change to a significant extent on passing into different solutions. In solution, a complicated mixture of forms under rapid equilibrium would also occur, (a) with respect to the position on the ring, being pseudoaxial or pseudoequatorial, and (b) with respect to the rotation about the *exo* C–C bond, being *trans* or *gauche*, thus resulting in the changes in the dipole moment of the *gauche* conformer. From Lennard-Jones–Pike analysis,[24] the internal energy difference between the two conformers, ΔE, is found to be 6.87 kJ mol^{-1}. This corresponds to a composition of 89% *trans* and 11% *gauche* at 25 °C.

Molecular orbital calculations of 1 and 2

It is instructive to first examine the *gauche–trans* equilibrium of the parent analogues of **1** and **2**, namely bi-1,3-dithianyl **3** and bi-1,3-dioxolanyl **4**, respectively. **4** has been studied by X-ray crystallography, IR and NMR spectroscopy.[5,6] In the solid state, it exists as the *anti*-ee conformation. However, it exists predominantly in a polar *gauche* form in solution. We have calculated the energy difference between the *gauche* and *trans* conformations of **4** using various levels of *ab initio* and DFT theories (Table 4). All theoretical methods predict a preference for the *gauche* rotamer. *Ab initio* methods predict an energy difference (ΔE) of ~10 kJ mol^{-1}, while the DFT methods lead to a smaller energy difference (~5 kJ mol^{-1}). At our best level of theory, the QCISD(T)/6-311+G(2df,p) level, the *gauche* rotamer is more stable than the *trans* form by 5.4 kJ mol^{-1}. The calculated enthalpy difference (ΔH) and free energy difference (ΔG) are summarised in Table 4. The ΔH value was obtained by adding zero-point energy correction, Δ(ZPE), and the thermal correction ($H_T - H_0$) to ΔE; and the ΔG value was computed

from the equation $\Delta G = \Delta H - T\Delta S$, where ΔS is the entropy change. Our theoretical estimate of the *gauche–trans* free energy difference at 298 K (ΔG_{298}) is 2.0 kJ mol^{-1}. This finding is consistent with the observation of a polar form in the solution phase.[5] The calculated dipole moment of the *gauche* form is 7.41×10^{-30} C m (B3-LYP/6-31G*), in good agreement with the experimental estimate of 6.87×10^{-30} C m.[5] It is worth noting that the calculated infrared spectra of both *trans* and *gauche* forms (Table S1) are in excellent accord with the experiment. This suggests that the observed polar form corresponds to the calculated *gauche* conformation. It is important to note that the ΔE value obtained from B3-LYP/6-311+G(2d,p) calculations (Table 4) is in excellent accord with our best ΔE value calculated at the QCISD(T)/6-311+G(2df,p) level. This lends confidence to our predicted values for the larger phenyl substituted systems (*i.e.* **1** and **2**).

As with **4**, the *gauche* form is more stable than the *trans* structure in **3**. However, the calculated energy difference (ΔE) is very small, 0.9 kJ mol^{-1} [QCISD(T)/6-311+G(2df,p)]. Again, the calculated entropy term favours the *trans* rotamer. As a result, there is a reversal of the *gauche–trans* equilibrium for the calculated free energy difference (Table 4). At 298 K, the calculated free energy (ΔG_{298}) favours the *trans* rotamer by 1.5 kJ mol^{-1}. We are not aware of any experimental study for this system.

For the larger phenyl-substituted systems (**1** and **2**), their *gauche–trans* equilibria were examined at the B3-LYP/6-311+G(2d,p) level (Table 5). In sharp contrast to the parent analogue **4**, the *trans* rotamer is the preferred structure in **2**, $\Delta E = 3.1$ kJ mol^{-1}. At 298 K, the calculated free energy difference (ΔG_{298}) in the gas phase is 5.7 kJ mol^{-1}. This calculated strong preference of the *trans* form is in good accord with the experimental observations in liquid and solid phases. The calculated ΔG_{298} agrees well with the experimental values in benzene and carbon tetrachloride solutions. For the *gauche* rotamer, the calculated dipole moment (6.91×10^{-30} C m) is in close agreement with the experimental estimate.

For the sulfur-containing system, the *gauche* preference is maintained in the phenyl-substituted system **1**. The calculated ΔE values are larger than the corresponding values in **3** (Tables 4 and 5). The best estimate of ΔE is 6.5 kJ mol^{-1}. The calculated free energy at 298 K (ΔG_{298}) reduces slightly to 4.6 kJ mol^{-1}. Thus, theory predicts **1** to exist predominantly as the *gauche* form in an isolated state (corresponding to the gas phase). However, the *trans* structure was observed in liquid and solid phases. How does one account for the discrepancy between theory and experiment? One possible explanation is the larger barrier for internal rotation in **1**. We have examined the rotational barriers of **1–4** at the B3-LYP/6-311+G(2d,p) + ZPE level. Both the parent analogues (**3** and **4**) are predicted to have a small rotational barrier (15.6 and 15.4 kJ mol^{-1}, respectively). On the other hand, a significantly higher rotational barrier is calculated for the phenyl-substituted systems, 65.0 and 30.1 kJ mol^{-1} for **1** and **2**, respectively. In the case of **1**, the high barrier for interconversion of the *trans* and *gauche* rotamers suggests that it is difficult for **1** to achieve a rotational equilibrium at room temperature.

The calculated geometries of **1** and **2** (B3-LYP/6-31G*, Table 6) are in good accord with the X-ray structural data (Tables 1 and 3). There are some interesting structural features of **1–4** which warrant discussion. Firstly, we note that there is a significant increase of the central C–C bond length, by 0.04–0.07 Å (Table 6) upon phenyl substitution (*i.e.* **3→1** and **4→2**). The C–C lengthening is greater for the sulfur systems. Secondly,

Table 4 Calculated *gauche–trans* energy difference^a (kJ mol^{-1}) for **3**^{b} and **4**^{b}

Level	3	4
HF/6-31G*	−2.3	−8.5
MP2/6-31G*	−2.5	−12.9
MP3/6-31G*	−2.3	−11.9
MP4/6-31G*	−2.4	−12.6
QCISD/6-31G*	−2.5	−11.8
QCISD(T)/6-31G*	−2.3	−12.1
MP2/6-311G**	−4.8	−13.4
MP2/6-311+G(2d,p)	−1.9	−9.8
MP2/6-311+G(2df,p)	−1.1	−9.9
B3-LYP/6-31G*	−0.9	−7.5
B3-LYP/6-311G**	−0.8	−9.9
B3-LYP/6-311+G(2d,p)	−0.7	−4.9
B3-LYP/6-311+G(2df,p)	−0.6	−4.9
QCISD(T)/6-311+G(2df,p)^c	−0.9	−5.4
Δ(ZPE)^d	0.1	1.5
$\Delta(H_{298} - H_0)$	−0.1	−0.4
ΔH_0^{e}	−0.8	−3.9
ΔH_{298}^{e}	−0.9	−4.3
ΔG_{298}^{e}	1.5	−2.0

^{a} ΔE ($E_g - E_t$) values, unless otherwise noted. ^{b} Based on B3-LYP/6-31G* optimised geometry. ^{c} Estimated from additivity approximation: QCISD(T)/6-311+G(2df,p) = QCISD(T)/6-31G* + MP2/6-311+G(2df,p) − MP2/6-31G*. ^{d} B3-LYP/6-31G* values, scaled by 0.9804. ^{e} $\Delta H_0 = \Delta E$(QCISD(T)/6-311+G(2df,p)) − Δ(ZPE); $\Delta H_{298} = \Delta H_0 + (H_{298} - H_0)$; and $\Delta G_{298} = \Delta H_{298} - (298\Delta S)$.

Table 5 Calculated *gauche–trans* energy difference^a (kJ mol^{-1}) for **1**^{b} and **2**^{b}

Level	1	2
HF/6-31G*	−6.4	3.3
B3-LYP/6-31G*	−5.5	2.8
B3-LYP/6-311+G(2d,p)	−6.5	3.1
Δ(ZPE)^c	0.1	1.7
$\Delta(H_{298} - H_0)$	−0.1	2.2
ΔH_0^{d}	−6.4	4.8
ΔH_{298}^{d}	−6.3	7.0
ΔG_{298}^{d}	−4.6	5.7

^{a} ΔE values ($E_g - E_t$), unless otherwise noted. ^{b} Based on B3-LYP/6-31G* optimised geometry. ^{c} B3-LYP/6-31G* values, scaled by 0.9804. ^{d} $\Delta H_0 = \Delta E$(B3-LYP/6-311+G(2d,p)) − Δ(ZPE); $\Delta H_{298} = \Delta H_0 + (H_{298} - H_0)$; and $\Delta G_{298} = \Delta H_{298} - (298\Delta S)$.

Table 6 Calculated dipole moments (μ/D^a) and structural parameters^b for **1–4**

Species	μ	r(C–C)	$\angle$RCC	τRCCR	C–X^c	φ^{d}
trans **3** (R = H)	0.00	1.539	109.1	180.0	1.850, 1.950	
gauche **3** (R = H)	2.01	1.534	106.9	64.0	1.843, 1.849	
trans **1** (R = C$_6$H$_5$)	0.00	1.607	113.1	180.0	1.879, 1.879	90.0
gauche **1** (R = C$_6$H$_5$)	1.80	1.608	111.6	68.0	1.878, 1.879	91.0
trans **4** (R = H)	0.20	1.532	109.4	176.7	1.414, 1.421	
gauche **4** (R = H)	2.22	1.540	108.7	62.4	1.413, 1.420	
trans **2** (R = C$_6$H$_5$)	0.22	1.570	112.3	176.0	1.419, 1.427	91.3
gauche **2** (R = C$_6$H$_5$)	2.07	1.574	113.4	56.4	1.424, 1.427	80.2

^{a} 1 D = 3.337×10^{-30} C m. ^{b} B3-LYP/6-31G* level; bond lengths in Å and angles in degrees. ^{c} The two C–X bonds directly bonded to the central C–C bond; heteroatom X = O (**1** and **3**) and S (**2** and **4**). ^{d} Torsion angle between the phenyl ring and the central C–C bond.

a comparison of the CCR angles, R = H (**3** and **4**) and C_6H_5 (**1** and **2**) indicates that phenyl substitution in **3** and **4** leads to an increase of the RCC angle, by 3–5° (Table 6). The changes of C–C bond lengths and CCR angles may be attributed to a repulsive interaction between the two phenyl groups in **1** and **2**. Interestingly, the Ph–C–C–Ph torsional angle in **1** (68°) is substantially larger than in **2** (56°). Finally, we note that the two sets C–X bonds directly bonded to the central C–C bond are significantly different in their bond lengths for the *trans* structures (Table 6).

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