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Conformational Analysis of (±)-(1,1′-Biindene)-3,3′-dione, 2,2′,3,3′-Tetrahydro-(1,1′-binaphthalene)-4,4′(1*H*,1′*H*)-dione, and (1,1′-Bibenzosuberene)-5,5′-dione

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The dipole moments of (±)-(1,1′-biindene)-3,3′-dione **1**, (±)-2,2′,3,3′-tetrahydro-(1,1′-binaphthalene)-4,4′(1*H*,1′*H*)-dione **2**, and (±)-(1,1′-bibenzosuberene)-5,5′-dione **3** in carbon tetrachloride and benzene were measured over a range of temperatures. Analyses of the relative permittivity data in carbon tetrachloride and benzene showed that at 25 °C, **1** exists predominantly in the *gauche* conformation, whilst **2** and **3** favor the *trans* form. The experimentally derived values of the energy difference between the *gauche* and *trans* rotamers and the *gauche*/*trans* population quotient were compared with values predicted by molecular-orbital calculations. The crystal and molecular structures of **2** and **3** were determined by single-crystal X-ray diffraction methods. Both compounds exist in the *trans* conformation in the solid-state. Dynamic ^{1}H NMR was employed to **3** in order to determine the activation parameters for the barriers to rotation in solution.

During the last two decades, there has been a constant progression of knowledge concerning the stereochemical and conformational properties of various aromatic cyclic ketones.[1–4] In contrast, few studies have been concerned with the conformational preferences of the dimeric form, the bicyclic diones,[5,6] which are potential structural candidates in the design of supramolecular systems. For a compound to be used in constructing supramolecular systems, it is important to learn how to control its conformation. In order to understand the influence of the cycloalkyl moiety on the structure and the relative stability of the *trans* and *gauche* rotamers, we initiated a systematic study of these compounds, and now report on our findings concerning (±)-(1,1′-biindene)-3,3′-dione **1**, (±)-2,2′,3,3′-tetrahydro-(1,1′-binaphthalene)-4,4′(1*H*,1′*H*)-dione **2**, and (±)-(1,1′-bibenzosuberene)-5,5′-dione **3** (Fig. 1), based on dipole moment determination, X-ray diffraction measurements, and molecular-orbital calculations.

Experimental

Preparation of Compounds. Compounds **1**, **2**, and **3** were synthesized by free-radical dimerization with *t*-butyl peroxide.[7] Materials for the synthesis were from commercial sources, and were 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). Free-radical dimerization favors the formation of the (±) isomer, which was obtained in predominantly higher proportions than the meso isomer. To our knowledge, compound **3** has not been reported previously.

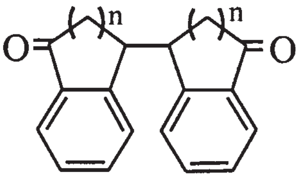

Fig. 1. Structure of **1**–**3** ($n = 1$–3).

(±)-(1,1′-Biindene)-3,3′-dione 1. To 1-indanone (2.00 g, 15.0 mmol) was added *t*-butyl peroxide (1.30 g, 8.9 mmol) and the reaction was gently refluxed under nitrogen for 3 days. The obtained brownish solution was concentrated, diluted with ether, washed with water, and purified by flash chromatography (hexane–ethyl acetate 6:1, $R_f = 0.20$) to give **1** as a pale-yellow solid (1.70 g, 43%): mp 193.0 °C (lit.[5] 191–192 °C). Found: C, 82.46; H, 5.48%; M$^+$, 262. Calcd for $C_{18}H_{14}O_2$ (MW 262): C, 82.42, H, 5.38%. δ_H (500 MHz; CD_2Cl_2; Me_4Si) 1.81–1.86 (2H, dd, $J =$ 3.46, 15.96 Hz, CH_2), 2.37–2.39 (2H, dd, $J = 7.63$, 11.79 Hz, CH_2), 4.18–4.22 (2H, m, C*H*), 7.73–7.68 (8H, m, aromatic-H).

(±)-2,2′,3,3′-Tetrahydro-(1,1′-binaphthalene)-4,4′(1*H*,1′*H*)-dione 2. The procedure for the preparation of **1** was used. α-Tetralone (2.20 g, 15.0 mmol) upon a reaction with *t*-butyl peroxide (1.30 g, 8.9 mmol) gave **2** as a white solid (1.65 g, 38%) after purification by chromatography (hexane–ethyl acetate 6:1, $R_f = 0.04$): mp 210.0 °C. Found: C, 82.43; H, 6.21%; M$^+$, 290. Calcd for $C_{20}H_{18}O_2$ (MW 290): C, 82.73, H, 6.25%. δ_H (500 MHz; CD_2Cl_2; Me_4Si) 1.92–2.18 (4H, m, CHCH_2CH_2), 2.67–3.11 (4H, m, CHCH_2CH_2), 3.22–3.26 (2H, m, C*H*), 7.38–8.08 (8H, m, aromatic-H).

(±)-(1,1′-Bibenzosuberene)-5,5′-dione 3. The procedure for the preparation of **1** was used. 1-Benzosuberone (2.40 g, 15.0 mmol) upon a reaction with *t*-butyl peroxide (2.60 g, 17.8 mmol) gave **3** as a white solid (1.48 g, 31%) after purification by chromatography (hexane–ethyl acetate 3:1, $R_f = 0.12$): mp 223.0 °C.

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Found: C, 82.60; H, 7.13%; M$^+$, 318. Calcd for $C_{22}H_{22}O_2$ (MW 318): C, 82.98, H, 6.97%. δ_H (500 MHz; CD_2Cl_2; Me_4Si) 1.44–1.64 (4H, m, $CHCH_2CH_2CH_2$), 1.68–1.88 (2H, m, $CHCH_2CH_2$), 1.92–2.25 (2H, m, $CHCH_2CH_2$), 2.42–2.58 (2H, m, $CHCH_2$), 2.64–2.75 (2H, m, $CHCH_2$), 3.20–3.35 (2H, m, CH), 6.52–7.50 (8H, m, aromatic-H).

Dipole Moment Determination. The relative permittivities were determined with a heterodyne-beat meter,[8] and the densities and refractive indices by standard procedures.[9] All of the solvents were carefully distilled and dried before use. The physical constants required for the relative permittivity have been given previously.[10,11]

X-ray Crystallography. Single crystals of **2** and **3** were obtained from benzene–hexane mixtures. The crystals were attached to glass fibres using epoxy glue, mounted on a Siemens SMART CCD system with Mo-Kα radiation. Data were collected using three ω-scans on each crystal over a 180° range at a fixed ϕ value of 54.74° with a 0.30° scan width and a 5 s count time per frame and a crystal-to-detector distance of 5.04 cm. Data were corrected for Lorentz and polarization effects with the SMART suite of programs,[12] and for the absorption effects with SADABS.[13] Structural solutions and refinements were carried out with the SHELXTL programs.[14] The structures were solved by direct methods, followed by full-matrix least-squares refinements. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at calculated positions. Crystal data of **2**: $C_{20}H_{18}O_2$, $M = 290.34$. Monoclinic, colorless blocks, $a = 15.6671(12)$ Å, $b = 7.3368(5)$ Å, $c = 14.0948(1)$ Å, $\beta = 112.1980(10)°$, $V = 1500.07(19)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_x = 1.286$ g/cm^3. Crystal dimension: $0.57 \times 0.49 \times 0.26$, μ(Mo-Kα) = 0.082 mm^{-1}, 9354 reflections measured, 3743 unique ($R_{int} = 0.0206$) which were used in all calculations. The final R and R_w were 4.55% and 11.31% (for $I > 2\sigma(I)$). Crystal data of **3**: $C_{22}H_{22}O_2$, $M = 318.40$. Monoclinic, colorless blocks, $a = 23.551(11)$ Å, $b = 7.927(3)$ Å, $c = 20.603(5)$ Å, $\beta = 121.10(2)°$, $V = 3294(2)$ Å^3, space group $C2/c$, $Z = 8$, $D_x = 1.284$ g/cm^3. Crystal dimension: $0.52 \times 0.40 \times 0.42$, μ(Mo-Kα) = 0.081 mm^{-1}, 10114 reflections measured, 4080 unique ($R_{int} = 0.0209$) which were used in all calculations. The final R and R_w were 4.61% and 10.69% (for $I > 2\sigma(I)$). Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.

Calculations. Theoretical geometrics, zero-point energies and dipole moments in the gas phases were obtained at the B3-LYP/6-31G(d) level of theory using the GAUSSIAN98 package of programs.[15] The initial geometries of **1**, **2**, and **3** were obtained from the crystal structures. Alternative forms were constructed from the crystal structures by adjusting the appropriate torsion angles. All of the structures were then allowed to optimize fully. The solvent effect on the structures was estimated by the Onsager model[15] at the B3-LYP/6-31G(d) level, using a dielectric constant of 2.2 for carbon tetrachloride and 78.4 for water. The cavity radii for species **1**, **2**, and **3** were 5.18, 5.41, and 5.61 Å, respectively. The relative energies were computed at the B3-LYP/6-311+G(d,p) level in the gas phase and at the B3-LYP/6-311+G(d,p) level with the Integral Equation Formalism version of Polarizable Continuum Method (IEFPCM) model.[15] Standard thermodynamic relations were applied to obtain the enthalpy (ΔH_{298}) and Gibbs free energy (ΔG_{298}).[16]

Dynamic NMR Measurement. All NMR spectra were recorded on a Bruker AMX-500 FTNMR spectrometer equipped with a variable temperature probe. CD_2Cl_2 was used as a solvent and tetramethylsilane as an internal standard.

Results and Discussion

Dipole Moment Measurements. The results of dipole moment measurements of **1**, **2**, and **3** are presented in Table 1 with the standard notation. Compound **3** had poor solubility in benzene, and thus only its dipole moment in carbon tetrachloride was measured. Three concentration dependencies, namely those of the relative permittivities, densities, and refractive indices ($\alpha\varepsilon_1$, βd_1, and γd_{12}), were determined for each solvent at the three temperatures. Using the least-squares method, the experimental values of the slope ($\alpha\varepsilon_1$, βd_1, and $\gamma {n_1}^2$; given by Eq. 1) at infinite dilutions of the compounds (w_2 denoting the solute weight fraction) and the respective molar polarization, refractions, and dipole moments were calculated. By measuring the dielectric effects in extremely dilute solutions of the compounds 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 Vines:[17]

$$\alpha\varepsilon_1 = \left(\frac{\delta\Delta\varepsilon}{\delta w_2}\right)_{w_2\to 0} \qquad \beta d_1 = \left(\frac{\delta\Delta d}{\delta w_2}\right)_{w_2\to 0}$$
$$\gamma {n_1}^2 = \left(\frac{\delta\Delta n^2}{\delta w_2}\right)_{w_2\to 0}. \tag{1}$$

(±)-(1,1′-Biindene)-3,3′-dione 1. The large dipole moments in carbon tetrachloride and benzene mean that the polar *gauche* rotamers must be present in high proportion in these solvents. From Table 1, it can also be seen that the dipole moment of the compound decreases with increasing temperature, indicating that the more polar *gauche* forms are more stable than the *trans* rotamer, and are higher in population. **1** can exist in two possible *gauche* forms, *gauche-a* and *gauche-b* (Fig. 2). Since **1** exists in the *gauche-a* conformation in the solid-state,[5] it is reasonable to assume that this sterically less-hindered rotamer would plausibly be the preferred *gauche* form in solution. The application of the Lennard-Jones–Pike method of analysis[18] to our dipole moment data yields ΔG ($= G_g - G_t$) and μ_g values of -3.67 kJ mol^{-1} and 5.95 D respectively. An alternative method for obtaining μ_g is to employ Eq. 2, where μ_o is the moment of the symmetrical half of the molecule (CR_2Y), α is the supplement of the central C–C–Y bond angle, and 2θ is the dihedral angle between the two C–C–Y planes.[19] In our calculations of **1**, μ_o was taken to be the dipole moment of 1-indanone with its direction along the C=O bond while the values of α (115.9°) and 2θ (35.6°) were determined from the X-ray diffraction data of the molecule.[5] Substitution of these values into the following equation gives a dipole moment (μ_g) of 6.03 D for the *gauche-a* rotamer, which is in good agreement with the value obtained by the Lennard-Jones–Pike method:

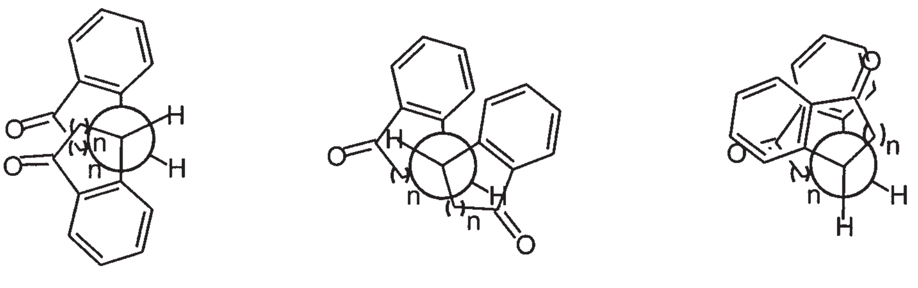
$$\mu(2\theta) = 2\mu_o \sin\alpha \cos\theta. \tag{2}$$

From the Boltzmann distribution, the corresponding *gauche* population in a carbon tetrachloride solution was found to be 81.5% at 25 °C. The high proportion of the *gauche* rotamer suggests that in **1**, the *gauche-a* conformation is inherently much more stable than the *trans*. This stability appears to

Table 1. Molar Polarization, Refractions, and Dipole Moments at Infinite Dilution of (±)-(1,1′-Biindene)-3,3′-dione **1**, 1-Indanone, (±)-2,2′,3,3′-Tetrahydro-(1,1′-binaphthalene)-4,4′(1*H*,1′*H*)-dione **2**, α-Tetralone, (±)-(1,1′-Bibenzosuberene)-5,5′-dione **3**, and 1-Benzosuberone

T/°C	Solvent	Conc. range /10^5 w_2	$\alpha\varepsilon_1$	β	γ	P_2/cm^3	R_D/cm^3	$\mu^{a)}$/D
a.	(±)-(1,1′-Biindene)-3,3′-dione **1** ($R_D = 74.56$ cm^3)							
25	CCl_4	210–400	18.15	−0.027	0.164	553.9	72.49	4.83 ± 0.02
45	CCl_4	180–360	15.21	−0.287		503.5		4.71 ± 0.01
60	CCl_4	140–280	13.75	−0.213		473.6		4.64 ± 0.02
25	Benzene	170–490	9.82	0.315	0.129	528.1	75.04	4.69 ± 0.02
45	Benzene	205–500	7.47	0.122		477.9		4.57 ± 0.01
60	Benzene	215–460	7.00	0.142		450.5		4.51 ± 0.02
b.	1-Indanone ($R_D = 38.31$ cm^3)							
25	CCl_4	390–905	18.60	−0.368	0.123	293.5	38.00	3.52 ± 0.01
25	Benzene	275–830	10.11	0.240	0.065	285.5	37.53	3.47 ± 0.02
c.	(±)-2,2′,3,3′-Tetrahydro-(1,1′-binaphthalene)-4,4′(1*H*,1′*H*)-dione **2** ($R_D = 83.86$ cm^3)							
25	CCl_4	150–350	3.36	−0.191	0.211	166.7	83.18	1.97 ± 0.01
45	CCl_4	160–300	3.72	−0.049		175.4		2.13 ± 0.01
60	CCl_4	160–340	4.01	−0.041		189.2		2.35 ± 0.02
25	Benzene	260–510	2.09	0.387	0.178	174.7	82.58	2.07 ± 0.02
45	Benzene	290–630	1.74	0.214		177.2		2.16 ± 0.01
60	Benzene	310–470	2.04	0.229		196.8		2.44 ± 0.02
d.	α-Tetralone ($R_D = 43.13$ cm^3)							
25	CCl_4	300–650	14.62	−0.349	0.144	262.6	42.25	3.26 ± 0.01
25	Benzene	290–725	8.03	0.236	0.104	258.9	44.11	3.22 ± 0.01
e.	(±)-(1,1′-Bibenzosuberene)-5,5′-dione **3** ($R_D = 93.16$ cm^3)							
25	CCl_4	200–300	7.86	−0.196	0.270	335.0	98.09	3.41 ± 0.01
45	CCl_4	200–350	7.42	−0.217		332.6		3.50 ± 0.01
60	CCl_4	200–320	7.14	−0.263		335.2		3.60 ± 0.02
f.	1-Benzosuberone ($R_D = 47.61$ cm^3)							
25	CCl_4	150–250	13.19	−0.412	−0.629	265.3	46.63	3.25 ± 0.01
25	Benzene	600–950	7.76	0.181	0.053	279.7	48.13	3.35 ± 0.01

a) $P_D = 1.05\ R_D$. 1 D = 3.337×10^{-30} C m.



gauche-a *trans* *gauche-b*

Fig. 2. Stable conformations of **1**–**3** (n = 1–3).

be a manifestation of the "*gauche* effect",[20] which states that there is a tendency for a structure which has the maximum number of *gauche* interactions between the adjacent electron pairs and/or polar bonds to be favored. In **1**, each carbonyl group possesses two electron pairs on each oxygen atom which enables the two carbonyl groups to form attractive interactions with one another. However, the final conformation adopted is still dependent on the overall balance of the attraction and repulsion between the groups in the molecule.

The dipole moment results of **1** in benzene are very similar to that in a carbon tetrachloride solution. This suggests that in benzene solution specific solute–solvent interactions, which

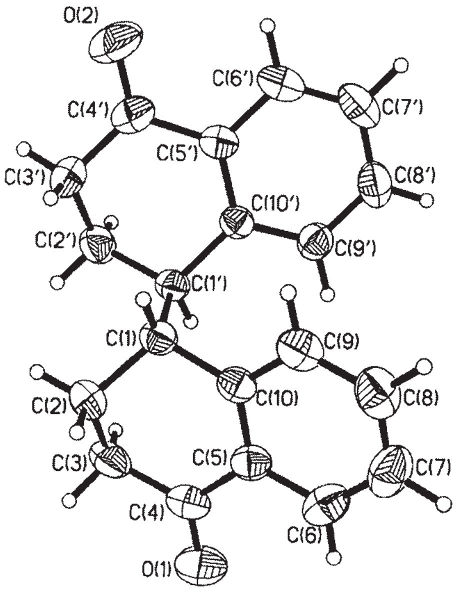


Fig. 3. Thermal ellipsoid diagram of **2**.

are observed in various analogous systems,[21,22] are plausibly absent. A Lennard-Jones–Pike analysis of the dipole moment data in benzene gives a *gauche* rotamer dipole moment of 5.65 D and a ΔG value of -3.54 kJ mol^{-1}. This corresponds to a population of 80.6% *gauche* and 19.4% *trans* rotamers at 25 °C.

2,2′,3,3′-Tetrahydro-(1,1′-binaphthalene)-4,4′(1*H*,1′*H*)-dione 2. An analysis of the data in Table 1 shows that, like **1**, the dipole moments obtained in carbon tetrachloride are very similar to that in benzene solutions. However, in contrast to **1**, the dipole moments in both carbon tetrachloride and benzene solutions increase with increasing the temperature, indicating that the *trans* rotamer is more stable than the *gauche*, and is higher in population in these solvents. The application of the Lennard-Jones–Pike method of analysis[18] to our dipole moment data yields ΔG and μ_g values of 8.33 kJ mol^{-1} and 7.73 D in carbon tetrachloride and 8.17 kJ mol^{-1} and 7.82 D in benzene solutions. From Eq. 2 (where μ_o was taken to be the dipole moment of α-tetralone with its direction along the C=O bond while the values of α (118.9°) and 2θ (173.1°) were determined from our X-ray diffraction data of **2**), μ_t was found to be 0.34 D. From the Boltzmann distribution, the corresponding *gauche* populations at 25 °C were found to be 6.3 and 6.8% in carbon tetrachloride and benzene, respectively.

(1,1′-Bibenzosuberene)-5,5′-dione 3. Table 1 shows that the dipole moment of this compound increases with increasing temperature in carbon tetrachloride solutions, indicating that, like in **2**, the *trans* rotamer is more stable than the *gauche* and is higher in population in these solvents. Analyses of our dipole moment data according to the Lennard-Jones–Pike method yield ΔG and μ_g values of 3.29 kJ mol^{-1} and 5.78 D. Based on our X-ray data of **3** and the dipole moment of 1-benzosuberone at 25 °C, μ_t was found to be 1.84 D and the corresponding percentage *gauche* population was obtained as 27.4% at 25 °C.

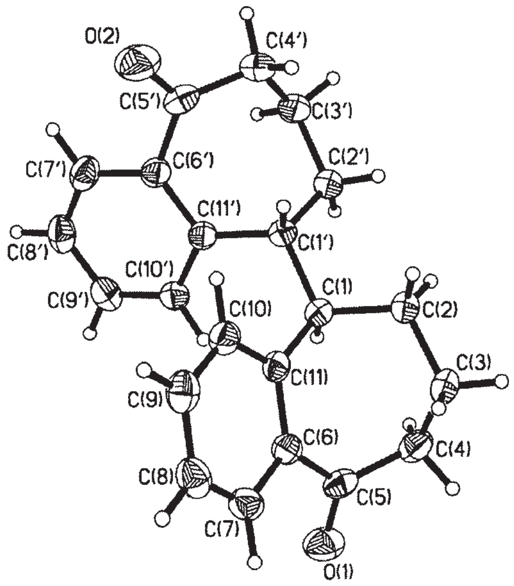


Fig. 4. Thermal ellipsoid diagram of **3**.

Table 2. Thermodynamic Quantities Governing the *Gauche*/*Trans* Equilibrium of **1**, **2**, and **3** in the Gas Phase[a)]

	1	**2**	**3**
ΔH_0[b)]/kJ mol^{-1}	−10	14.7	16.1
	(−7.2)	(17.3)	(12.9)
	[−13.1]	[23.4]	[10.4]
ΔH_{298}[b)]/kJ mol^{-1}	−8.4	14.3	14.6
	(−5.8)	(16.9)	(16.2)
	[−11.8]	[22.9]	[21.5]
ΔG_{298}[c)]/kJ mol^{-1}	−12.2	14.0	15.2
	(−9.0)	(16.5)	(17.2)
	[−14.4]	[22.5]	[22.5]
μ_g[d)]/Debye	5.34	4.73	4.36
	(6.08)	(5.26)	(4.70)
	[7.13]	[6.08]	[5.17]
ϕ[d)]/°	−59.0	68.3	90.6
	(−59.2)	(68.2)	(90.7)
	[−62.0]	[68.0]	[90.8]

a) The values of the corresponding parameters in CCl_4 and H_2O are enclosed in parenthesis and square brackets, respectively. b) Enthalpy difference, $\Delta H = H_{gauche} - H_{trans}$. c) Gibbs free energy difference, $\Delta G = \Delta G_{gauche} - \Delta G_{trans}$. d) Calculated at the B3-LYP/6-31G(d) level in the gas phase, and B3-LYP/6-31G(d)-Onsager level in CCl_4 and H_2O.

X-ray Crystallography. Molecules of **2** and **3** lie at general sites. Although the molecules do not have crystallographic symmetry, they show approximate two-fold rotational symmetry. Figs. 3 and 4 depict the structures and define the atomic numbering of **2** and **3**, respectively.

The crystal structure of **1** was reported earlier,[5] and the molecule was found to exist in the *gauche* form in the solid state. In contrast to **1**, molecules **2** and **3** exist in the *trans* conformation in the solid state with the central C–C bonds being 1.5641(17) Å and 1.5449(17) Å, respectively. Mislow et al[23] through studies on the bifluorenyl (central C–C bond = 1.542 Å) have indicated that clamped polyarylethanes, i.e., molecules where the aryl rings are constrained away from the central C–C bond so as to reduce steric interactions between the ends of

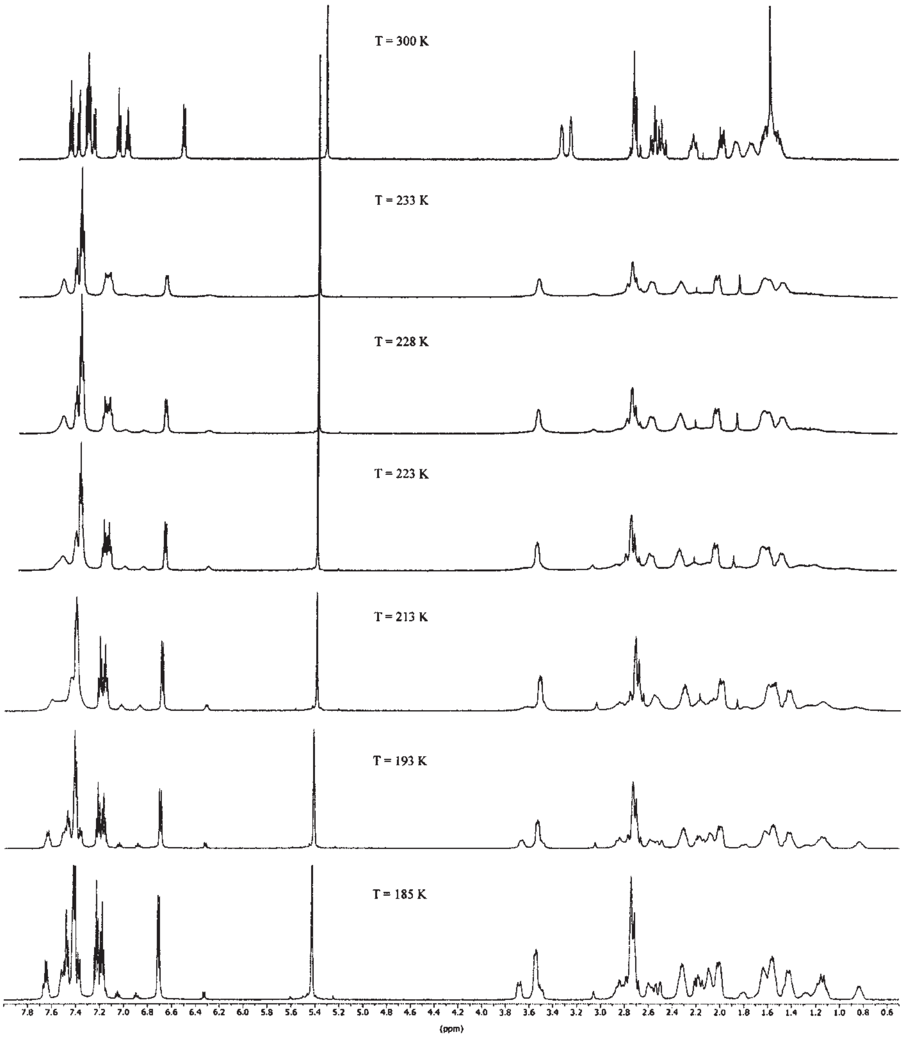


Fig. 5. Variable temperature ^{1}H NMR spectra of **3**.

the molecule, would favor the *gauche* rotamer as the *trans* rotamer experiences severe H···H repulsive interaction, since the hydrogens on the 1,8-position of one fluorenyl moiety are forced to point directly at the hydrogens in the 1′,8′-positions of the other fluorenyl ring. This rationale is not applicable in **2** and **3**, as it is noted that even though the aryl moieties in these molecules are in juxtapositions, the H(9) and H(9′) of **2** (H(9)···H(9′) distance is 3.384 Å) and the H(10) and H(10′) of **3** (H(10)···H(10′) distance is 3.727 Å) are located about the phenyl rings and are not pointing directly at one another.

In molecule **2**, the cyclohexenone rings adopt an envelope conformation with C(2) and C(2′) deviating by 0.347 and 0.652 Å from the C(1)C(10)C(5)C(4)C(3) and C(1′)C(10′)C(5′)C(4′)C(3′) planes, respectively. The phenyl moieties are coplanar with their fused cyclohexanone rings. In molecule **3**, the cycloheptenone rings are in the boat configuration with C(1)C(4)C(5) and C(1′)C(4′)C(5′) forming the tips of the boat and the phenyl groups are pointing in a direction opposite to the tips of the boat. The phenyl rings in molecules **2** and **3** are placed at 33.2° and 75.4° to each other.

Calculations. Our theoretical results were summarized in Table 2. We note here that for all three compounds the theoretical geometries are in excellent agreement when compared to the crystal structures. The average deviation of the key bond lengths, bond angles, and torsion angles between the non-hydrogen atoms is less than 0.01 Å, 0.4°, and 0.4°, respectively.

For compound **1**, our calculations suggest that in both the gas and solution phases, *gauche-a* is the most stable form. The calculated μ_g of 6.08 D is in excellent agreement with that determined experimentally. However, the calculated ΔG_{298} is somewhat too large when compared to the experimental value. As a result, our calculations predicted that compound **1** exists almost exclusively in the *gauche-a* form in CCl_4. This large calculated free-energy difference obtained could arise from the fact that the basis sets employed in the single-point calculations were too small. However, with the size of **1**, calculations with larger basis sets become prohibitive. For compound **2**, the calculated ΔG_{298} is 17 $kJ\,mol^{-1}$, in agreement with experiment that the *trans* form is dominant in CCl_4. The calculated μ_g and μ_t are 5.26 and 1.32 D, respectively, which are in qualitative agreement with the experiment. For compound **3**, again, the *trans* form is predicted to be more stable (by at least 15 $kJ\,mol^{-1}$), which is consistent with our experimental observations. The calculated dipole moment μ_t (2.49 Debye) is in good agreement with the experimental value of 1.84 Debye, but the theoretical μ_g is too small by ~1 Debye. From the calculations of compounds **2** and **3**, it is observed that the dipole moment of the *trans* form is at least two Debyes smaller than the corresponding *gauche* form. Thus, it is not surprising that the *trans* form would be the favored rotamer. However, the same rationale cannot be applied to explain the domination of the *gauche* form in **1** as μ_t is also smaller than μ_g for this compound. However, we note that this difference in the dipole moment of these two forms is comparatively smaller (~1 Debye), such that other competing factors involved could cause a reversal of the *trans* $\leftrightarrows$ *gauche* equilibrium. One possible factor may be attributed to the *gauche* effect (which was discussed earlier). Another plausible reason is the electrostatic interaction of the π rings. In the *trans* conformation, the π rings are situated closer to each other compared to the corresponding *gauche* form. Because this interaction is repulsive, and hence unfavourable, it could destabilise the *trans* form, thus leading to a change of the preferred conformation in **1**.

Dynamic NMR Measurements. Variable temperature ^{1}H NMR measurements were obtained for **1–3**. However, as the temperature decreased, only the signals in the spectrum of **3** broadened, coalesced and resharpened again to a well-resolved spectrum with the aromatic protons ranging from 7.67–6.32 ppm (Fig. 5). The low-temperature spectrum can be analyzed as two distinct subspectra arising from the exchange between the *trans* and *gauche* conformers. One of the two subspectra had H(10) and H(10′) which are significantly more shielded than the other; this is consistent with the *trans* ground-state conformation, where the phenyl ring is positioned within the shielding zone of its companion phenyl ring. Calculations of the activation parameters of **3** gave $\Delta S^\ddagger$, $\Delta H^\ddagger$ and $\Delta G^\ddagger{}_{228}$ values of -29.3 J mol^{-1} K^{-1}, 37.85 kJ mol^{-1} and 44.54 kJ mol^{-1}, respectively.

Conclusion

The conformational stabilities of **1–3** were studied by means of dipole moment determination, X-ray crystallography, and molecular orbital calculations. Dipole moment experiments and X-ray crystallography data showed that **1** preferred the *gauche* form, whilst **2** and **3** favored the *trans* conformation. Computational calculations at the B3-LYP/6-31G(d) level of theory were in line with the experimental findings. We have also demonstrated that H···H interactions are absent in the *trans* rotamers of this series of compounds. Thus, even though **1** exists predominantly in the *gauche* form, a further increase in the cycloalkyl ring size favors the *trans* conformation. **3** was shown to exist in a higher proportion of the *trans* conformer in solution than **2**.

References

1 S. Blanco, J. C. Lopez, A. B. Gomez, and J. L. Alonso, *Mol. Phys.*, **97**, 853 (1999).

2 P. Jin and T. A. Wildman, *J. Phys. Chem.*, **95**, 20 (1991).

3 R. J. Abraham and M. S. Lucas, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1269.

4 G. Bodennec and M. St-Jacques, *Can. J. Chem.*, **55**, 1199 (1997).

5 N. E. Heimer, M. Hojjatie, and C. A. Panetta, *J. Org. Chem.*, **47**, 2593 (1982).

6 H. H. Huang, *Aust. J. Chem.*, **29**, 2415 (1976).

7 K. K. Chiu and H. H. Huang, *J. Chem. Soc. B*, **1969**, 2758.

8 H. H. Huang and E. P. A. Sullivan, *Aust. J. Chem.*, **21**, 1721 (1968).

9 R. J. W. LeFevre, "Dipole Moments," 3rd ed, Methuen, London (1953), Chap. 2; *Adv. Phys. Org. Chem.*, **3**, 1 (1965).

10 K. E. Calderbank, R. J. W. LeFevre, and G. L. D. Ritchie, *J. Chem. Soc. B*, **1968**, 503.

11 L. H. L. Chia, H. H. Huang, and P. K. K. Lim, *J. Chem. Soc. B*, **1969**, 608.

12 "SMART, ver. 4.05," Siemens Energy & Automation Inc., Madison, WI (1996).

13 G. M. Sheldrick, "SADABS," University of Göttingen (1996).

14 "SHELXTL, ver. 5.03," Siemens Energy & Automation Inc., Madison, WI (1995).

15 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, "Gaussian 98, Revision A.6," Gaussian, Inc., Pittsburgh, PA (1998).

16 J. E. Del Bene, H. D. Mettee, M. J. Frisch, B. T. Luke, and J. A. Pople, *J. Phys. Chem.*, **87**, 3279 (1983).

17 R. J. W. LeFevre and H. Vine, *J. Chem. Soc.*, **1937**, 1805.

18 J. E. Lennard-Jones and H. H. M. Pike, *Trans. Faraday Soc.*, **30**, 830 (1934).

19 R. J. LeFevre and B. Orr, *Aust. J. Chem.*, **17**, 1098 (1964).

20 S. Wolfe, *Acc. Chem. Res.*, **5**, 102 (1972).

21 C. Reichardt, "Solvents and Solvent Effects in Organic Chemistry," 2nd ed, VCH, Germany (1988), pp. 110–115.

22 B. G. Tan, L. H. L. Chia, H. H. Huang, M. H. Kuok, and S. H. Tang, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 1407.

23 D. A. Dougherty, F. M. Llort, K. Mislow, and J. F. Blount, *Tetrahedron*, **34**, 1301 (1978).