# Conformational analysis of *meso*- and (±)-2,3-dicyano-2,3-dicyclopropylbutane and 1,2-dicyanotetracyclopropylethane†

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The dipole moments of *meso*-2,3-dicyano-2,3-dicyclopropylbutane *meso*-**1**, (±)-2,3-dicyano-2,3-dicyclopropylbutane (±)-**1** and 1,2-dicyanotetracyclopropylethane **2** in carbon tetrachloride and benzene have been measured over a range of temperatures. Analyses of the relative permittivity data show that at 25 °C, *meso*-**1** and (±)-**1** favour the *trans* form. However, replacement of the methyl groups in **1** with cyclopropyl moieties completely reverses the *trans* ⇌ *gauche* equilibrium, such that **2** exists in 74% *gauche* conformation. The experimentally derived values of the energy difference between the *gauche* and *trans* conformers and the *gauche*/*trans* population quotients were compared with values predicted by molecular orbital calculations. Theory predicts that the conformational preference of the substituted dicyanoethanes is strongly influenced by solvent polarity. The crystal and molecular structures of *meso*-**1** and **2** were determined by single-crystal X-ray diffraction methods. Both compounds exist in the *trans* conformation in the solid state.

## Introduction

Our interest in polar and steric effects on rotational isomerism in symmetrically substituted ethanes has led us to investigate the influence of the cyano group in such molecules. Earlier works on 1,2-dicyanoethane[1] have shown that this compound exists predominantly in the *gauche* form. However, studies on dicyano compounds containing phenyl and alkyl substituents[2–5] have shown that these compounds exists mainly in the *trans* conformation, with the exception of 9,9′-dicyano-9,9′-bifluorenyl, which favours the *gauche* configuration.[6] Cyclopropyl groups are known to exhibit peculiar chemical and physical properties that are significantly different from those of alkanes or cycloalkanes. They have been shown to exhibit double bond character, qualifying them as "functional carbon groups".[7] We now report our findings on *meso*-2,3-dicyano-2,3-dicyclopropylbutane *meso*-**1** (±)-2,3-dicyano-2,3-dicyclopropylbutane (±)-**1** and 1,2-dicyanotetracyclopropylethane **2** based on dipole moment determinations, X-ray diffraction measurements and molecular orbital calculations.

## Experimental

Reagents for the syntheses were purchased from Aldrich and used without further purification. $^1$H NMR spectra were recorded on a Bruker Advance DRX500 spectrometer. Elemental analyses were determined with a Perkin-Elmer PE 2400 CHN elemental analyser and melting points were measured using a Thomas Hoover capillary melting point apparatus and are uncorrected.

### Preparation of compounds

**2,3-Dicyano-2,3-dicyclopropylbutane.** 2,3-Dicyano-2,3-dicyclopropylbutane **1**, was prepared from methyl cyclopropyl ketone by the method of Overberger and Lebovits.[8] The reaction mixture obtained was concentrated to yield a yellow oil which upon recrystallisation with hexane gave *meso*-**1** as a white solid (1.62 g, 44% based on methyl cyclopropyl ketone); mp 41 °C. Found: C, 76.66; H, 8.68; N, 14.90%. $C_{12}H_{16}N_2$ (mw 188) requires: C, 76.70; H, 8.51; N, 14.89%. $\delta_H$ (500 MHz; $CD_2Cl_2$; $Me_4Si$) 1.63 (s, 6H), 1.19–1.13 (m, 2H), 0.81–0.74 (m, 4H), 0.69–0.62 (m, 2H), 0.51–0.45 (m, 2H). The residual solution was purified by flash chromatography over silica gel (hexane) to yield (±)-**1** as a colourless oil (0.85 g, 23% based on methyl cyclopropyl ketone). Found: C, 76.42; H, 8.50; N, 14.76%. $C_{12}H_{16}N_2$ (mw 188) requires: C, 76.70; H, 8.51; N, 14.89%. $\delta_H$ (500 MHz; $CD_2Cl_2$; $Me_4Si$) 1.56 (s, 6H), 1.17–1.11 (m, 2H), 0.80–0.75 (m, 4H), 0.68–0.62 (m, 2H), 0.51–0.46 (m, 2H).

**1,2-Dicyanotetracyclopropylethane.** 1,2-Dicyanotetracyclopropylethane **2** has previously been prepared in two steps by the reaction of bis(dicyclopropylmethylene)hydrazine **3** with anhydrous hydrogen cyanide.[9] Due to difficulties in obtaining hydrogen cyanide, we decided to use sodium cyanide and herein report the direct synthesis of **2** from **3**.

Compound **3** was prepared from dicyclopropyl ketone by the method of Bernlöhr and co-workers.[9] To a solution of compound **3** (2.16 g, 10.0 mmol) in pentane (15 ml) was added an ethanolic solution of sodium cyanide (4.41 g, 90.0 mmol) and the mixture stirred vigorously. Concentrated HCl (7.46 ml, 90 mmol) was added dropwise[10] and the mixture was stirred for 8 days at 52 °C. The brown solution obtained was concentrated, diluted with diethyl ether, washed with $H_2O$ and purified by silica gel chromatography (hexane–

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† Electronic supplementary information (ESI) available: **Table S1** Calculated geometries of *meso*-**1**, (±)-**1**, **2** and **4**. see http://www.rsc.org/suppdata/nj/b1/b103740b/

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dichloromethane 3 : 1 and 1,2-dichloroethane) to give **2** as a light yellow solid (0.86 g, 36%), mp 73 °C (lit.[9] 77–78 °C). Found: C, 79.87; H, 8.52; N, 11.46%. $C_{16}H_{20}N_2$ (mw 240) requires: C, 79.96; H, 8.39; N, 11.65%. $\delta_H$ (500 MHz; $CDCl_3$; $Me_4Si$) 1.32–1.27 (m, 4H), 0.82–0.77 (m, 4H), 0.71–0.60 (m, 12H).

### 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.[4,13]

### Crystal structure determination and refinement

Single crystals of *meso*-**1** were obtained from hexane and of **2** from benzene–hexane.

Crystal data for *meso*-**1**: $C_{12}H_{16}N_2$, $M = 188.27$, monoclinic, colourless prisms, $a = 7.3831(7)$, $b = 8.2193(8)$, $c = 9.7902(9)$ Å, $\beta = 100.292(2)°$, $V = 584.6(1)$ Å$^3$, space group $P2_1/n$, $Z = 2$, $D_x = 1.070$ g cm$^{-3}$, crystal dimensions: 0.40 × 0.30 × 0.30 mm, $\mu$(Mo-K$\alpha$) = 0.064 mm$^{-1}$, 2748 reflections measured, 1023 unique ($R_{int} = 0.0292$) which were used in all calculations. The final $R$ and $R_w$ were 5.99 and 18.17%, respectively, [for $I > 2\sigma(I)$].

Crystal data for **2**: $C_{16}H_{20}N_2$, $M = 240.34$, monoclinic, colourless prisms, $a = 7.0406(3)$, $b = 14.7756(4)$, $c = 6.9714(3)$ Å, $\beta = 104.185(1)°$, $V = 703.12(5)$ Å$^3$, space group $P2_1/c$, $Z = 2$, $D_x = 1.135$ g cm$^{-3}$. Crystal dimensions: 0.50 × 0.46 × 0.40 mm, $\mu$(Mo-K$\alpha$) = 0.067 mm$^{-1}$, 4330 reflections measured, 1728 unique ($R_{int} = 0.0227$) which were used in all calculations. The final $R$ and $R_w$ were 4.38 and 11.79%, respectively, [for $I > 2\sigma(I)$].

Data collections were performed at room temperature using a Siemens R3m/V200 diffractometer with Mo-K$\alpha$ radiation ($\lambda = 0.710\,60$ Å). Lorentz and polarization corrections, structure solution by direct methods, full-matrix least-squares refinements and preparation of figures were all performed by programs in the SHELXTL-Plus PC program package.[14] All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at calculated positions and assigned isotropic displacement coefficients 1.6 times that of the atom to which they are attached.

CCDC reference numbers 164827 and 164828. See http://www.rsc.org/suppdata/nj/b1/b103740b/ for crystallographic data in CIF or other electronic format.

### Molecular orbital calculations

Standard *ab initio* and density functional calculations were carried out using the GAUSSIAN 98 series of programs.[15] Geometry optimizations were performed at the B3-LYP[16] level using the split-valence polarized 6-31G* basis set.[17] Higher-level relative energies were computed at the B3-LYP/6-311+G** level, using the B3-LYP/6-31G* optimized geometries and including the zero-point energy (B3-LYP/6-31G* value, scaled by a factor of 0.9804).[18] For 1,2-dicyanoethane, the *gauche*/*trans* equilibrium was also investigated at the G3(MP2) theory.[19] In the present study, we have employed the Onsager's self-consistent reaction field (SCRF) theory[20] at the dipole level to examine the solute–solvent interaction. The cavity radii were derived from the calculated molecular volumes, computed using a Monte Carlo method at the HF/6-31G* level.[21] The calculated *gauche*/*trans* energy differences ($\Delta H_0$) for various compounds are summarized in Table 3. The free energy differences ($\Delta G$) were computed from the equation $\Delta G_T = \Delta H_T - T\Delta S$, where $\Delta S$ is the entropy change and $\Delta H_T = \Delta H_0 + (H_T - H_0)$.

## Results and discussion

### Dipole moment measurements

The results of the dipole moment measurements of *meso*-**1**, (±)-**1** and **2** are presented in Table 1 with standard notation. Three concentration dependencies, namely those of the relative permittivities, densities and refractive indices ($\alpha\varepsilon_1$, $\beta d_1$ and $\gamma d_{12}$) were determined for each solvent at the three temperatures. Using the least squares method, the experimental values of the slopes $\alpha\varepsilon_1$, $\beta d_1$ and $\gamma n_1{}^2$ [given by eqn. (1)] at infinite dilutions of the compounds ($w_2$ denoting the solute weight fraction) and the respective molar polarisation, refractions and dipole moments were calculated.

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

By measuring the dielectric effects in extremely dilute solutions of the compounds in non-polar solvents like carbon

**Table 1** Molar polarization, refractions and dipole moments at infinite dilution of *meso*-2,3-dicyano-2,3-dicyclopropylbutane *meso*-**1**, (±)-2,3-dicyano-2,3-dicyclopropylbutane (±)-**1** and 1,2-dicyanotetracyclopropylethane **2**

| | $T$/°C | Solvent | Conc. range ($10^5\ w_2$) | $\alpha\varepsilon_1$ | $\beta$ | $\gamma$ | $P_2$/cm$^3$ | $R_D$/cm$^3$ | $\mu^a/10^{-30}$ C m |
|---|---|---|---|---|---|---|---|---|---|
| *meso*-**1** ($R_D$ = 53.305 cal) | 7 | $CCl_4$ | 230–485 | 4.04 | −0.618 | | 133.4 | | 6.41 ± 0.03 |
| | 25 | $CCl_4$ | 260–560 | 4.09 | −0.591 | 0.022 | 136.4 | 53.08 | 6.74 ± 0.02 |
| | 45 | $CCl_4$ | 240–565 | 3.93 | −0.729 | | 141.7 | | 7.14 ± 0.04 |
| | 7 | Benzene | 298–602 | 3.93 | 0.068 | | 193.7 | | 8.37 ± 0.04 |
| | 25 | Benzene | 266–590 | 3.84 | 0.140 | −0.003 | 191.2 | 54.14 | 8.55 ± 0.03 |
| | 45 | Benzene | 240–571 | 3.63 | 0.142 | | 198.3 | | 8.75 ± 0.04 |
| (±)-**1** ($R_D$ = 53.305 cal) | 7 | $CCl_4$ | 240–500 | 5.27 | −0.557 | | 155.1 | | 7.22 ± 0.02 |
| | 25 | $CCl_4$ | 540–750 | 5.54 | −0.530 | 0.028 | 163.2 | 53.37 | 7.65 ± 0.02 |
| | 45 | $CCl_4$ | 230–640 | 5.21 | −0.607 | | 164.1 | | 8.01 ± 0.03 |
| | 7 | Benzene | 410–900 | 4.83 | 0.176 | | 217.2 | | 9.09 ± 0.04 |
| | 25 | Benzene | 330–725 | 4.57 | 0.142 | −0.004 | 216.5 | 53.19 | 9.43 ± 0.02 |
| | 45 | Benzene | 310–775 | 4.50 | 0.158 | | 220.5 | | 9.76 ± 0.03 |
| **2** ($R_D$ = 67.784 cal) | 7 | $CCl_4$ | 150–400 | 8.32 | −0.741 | | 281.4 | | 10.37 ± 0.02 |
| | 25 | $CCl_4$ | 200–430 | 7.57 | −0.635 | 0.055 | 264.8 | 71.53 | 10.26 ± 0.02 |
| | 45 | $CCl_4$ | 220–420 | 6.34 | −0.763 | | 246.5 | | 10.07 ± 0.03 |
| | 7 | Benzene | 400–900 | 5.94 | 0.228 | | 321.5 | | 11.31 ± 0.04 |
| | 25 | Benzene | 330–800 | 5.18 | 0.180 | 0.047 | 301.3 | 71.55 | 11.19 ± 0.02 |
| | 45 | Benzene | 380–700 | 4.16 | 0.096 | | 270.7 | | 10.74 ± 0.03 |

[a] $P_D = 1.05R_D$

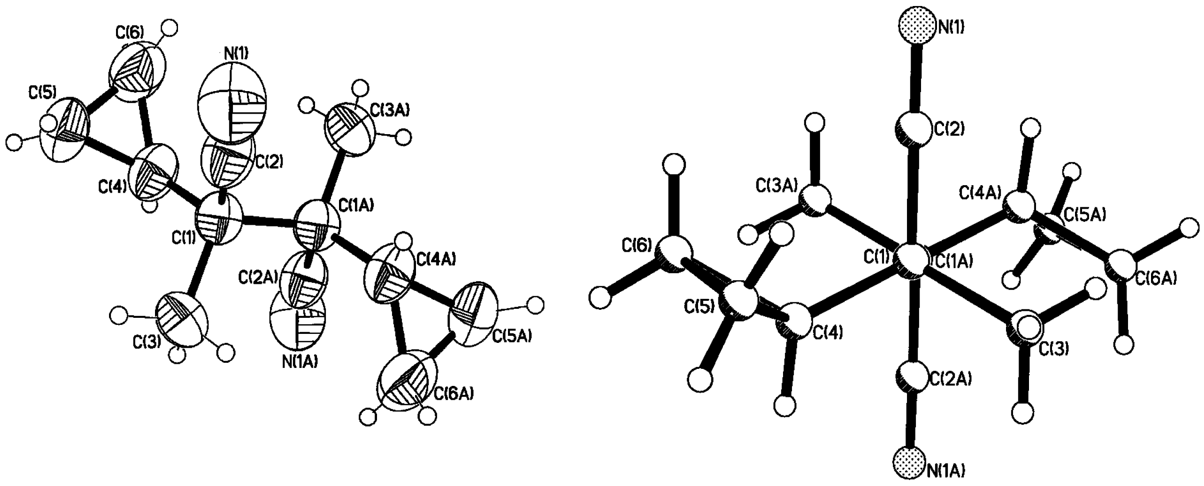

**Fig. 1** Thermal ellipsoid and Newman projection diagrams of *meso*-**1**.

tetrachloride and benzene, we can 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.[12,22]

***meso*-2,3-Dicyano-2,3-dicyclopropylbutane *meso*-1.** Table 1 shows that the dipole moment of this compound increases with increasing temperature in both carbon tetrachloride 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[23] to our dipole moment data in carbon tetrachloride yields a $\Delta E(= E_g - E_t)$ value of 5.21 kJ mol$^{-1}$ and a *gauche* conformer dipole moment ($\mu_g$) of $15.26 \times 10^{-30}$ C m.

Assuming that $\mu_g$ 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 and $\mu_g$ values yields a population of 19% *gauche* and 81% *trans* at 25 °C.

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

Lennard-Jones–Pike analysis of the dipole moment data in benzene gives a *gauche* conformer dipole moment of $13.74 \times 10^{-30}$ C m and $\Delta E$ value of 2.86 kJ mol$^{-1}$. This corresponds to a population of 38% *gauche* and 62% *trans* conformers at 25 °C. These results are comparable with 2,3-dicyano-2,3-dimethylbutane, which exists in carbon tetrachloride and benzene as 18 and 43% *gauche* conformation, respectively.[4] Since the dielectric constants of carbon tetrachloride and benzene are similar in value, the larger *gauche* population indicated in benzene is consistent with earlier observations that polar solutes and aromatic solvents interact to form weak complexes and when rotational isomers are involved, there is a tendency for specific solvent interactions to be established with the more polar isomer.[24] The preferential stabilization of the *gauche* conformer is explicable in terms of the *gauche* configuration having two cyano groups closer together. The π-electron cloud of benzene would interact with these polar groups in the region away from the bulkier cyclopropyl and methyl moieties. Compared with the *gauche* conformer, the *trans* form would have the cyano groups "sandwiched" between the cyclopropyl and methyl moieties and thus cause hindrances during π-complex formation.

It is interesting to compare the results of *meso*-**1** with those found in other members of the *meso*-2,3-dicyano-2,3-dicycloalkylbutane series ($n = 5$, 6).[2,3] In carbon tetrachloride, where no specific solute–solvent interactions are expected, the *gauche* population is 26% for *meso*-2,3-dicyano-2,3-dicyclopentylbutane and decreases to 16% in *meso*-2,3-dicyano-2,3-dicyclohexylbutane. However, in benzene, the results of *meso*-**1** contrast with those of *meso*-2,3-dicyano-2,3-dicyclopentylbutane and *meso*-2,3-dicyano-2,3-dicyclohexylbutane. In the latter two compounds, the dipole moment decreases with increasing temperatures, indicating that the *gauche* conformer is more stable than the *trans* form in this solvent. This observation further confirms the stabilization effect of benzene on the *gauche* conformer.

**(±)-2,3-Dicyano-2,3-dicyclopropylbutane (±)-1.** The dipole moments of (±)-**1** in carbon tetrachloride and benzene are higher than those of *meso*-**1** in the corresponding solvents. This is similar to the behaviour of most *meso*/(±) diastereoisomers, including that of 2,3-dicyano-2,3-dicyclopentylbutane and 2,3-dicyano-2,3-dicyclohexylbutane.[2,3]

Analysis of the data in Table 1 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 method of analysis[23] to our dipole moment data yields $\Delta E$ values of 4.48 and 3.83 kJ mol$^{-1}$ in carbon tetrachloride and benzene, respectively, and the percentage *gauche* population at 25 °C was found to be 25% in carbon tetrachloride and 30% in benzene. These results contrast with (±)-2,3-dicyano-2,3-dicyclopentylbutane and (±)-2,3-dicyano-2,3-dicyclohexylbutane which exist predominantly as the *trans* conformer in carbon tetrachloride but prefer the *gauche* configuration in benzene solution.[2,3]

**1,2-Dicyanotetracyclopropylethane 2.** The large dipole moments in carbon tetrachloride and benzene means that the polar *gauche* conformer 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 *gauche* conformer is more stable than the *trans*, and is higher in population.

Application of Lennard-Jones–Pike analysis[23] to our dipole moment data in carbon tetrachloride yields a $\Delta E$ value of 4.33 kJ mol$^{-1}$ and a *gauche* conformer dipole moment ($\mu_g$) of $11.90 \times 10^{-30}$ C m. From eqn. (2), the percentage *gauche* population at 25 °C was found to be 74%. These results contrast with **1**, which favours the *trans* isomer when it is in carbon tetrachloride and benzene solutions. This difference in conformation behaviour can be understood on the basis of the *trans* $\rightleftharpoons$ *gauche* equilibrium; the balance between steric, electrostatic and stereoelectronic factors. The *trans* form possesses two alkyl···alkyl interactions, whereas the *gauche* form contains three such interactions. Notwithstanding these steric repulsions, the *gauche* conformer becomes the preferred isomer when the methyl moieties are replaced by the planar cyclopropyl groups. Since **2** exists in the *trans* conformation in the solid state (as shown by our X-ray data), the preference for the *gauche* conformer in solution may plausibly be attributed to the greater solvent stabilization of the polar rotamer in **2** so as to reverse the *trans* ⇌ *gauche* equilibrium, even in nonpolar solvents like carbon tetrachloride and benzene.

## X-Ray structure determination

Bond lengths, bond angles and torsion angles based on the final atomic positions are shown in Table 2. Fig. 1 and 2 depict the structures and define the atomic numbering of *meso*-**1** and **2**, respectively.

Molecules of *meso*-**1** and **2** exist in the *trans* conformation in the crystalline state. This is similar to *meso*-2,3-dicyano-2,3-dicyclopentylbutane[2] and *meso*-2,3-dicyano-2,3-dicyclohexylbutane,[3] which also adopt the *trans* conformation in the solid state. The bond lengths and angles of **2** compare well with the corresponding ones of *meso*-**1**. The cyclopropyl rings in both molecules adopt a propeller-like arrangement with the C(6)–C(4)–C(1)–C(1A) angle of *meso*-**1** being 88.6(1)°, and the C(4)–C(2)–C(1)–C(1A) and C(7)–C(5)–C(1)–C(1A) angles of **2** being 85.3(2) and 87.8(2)°, respectively.

**Table 2** Bond lengths, bond angles and torsion angles of *meso*-**1** and **2**[a]

| *meso*-**1** | | **2** | |
|---|---|---|---|
| N(1)–C(2) | 1.138(3) | C(1)–C(8) | 1.480(2) |
| C(1)–C(1A) | 1.576(4) | C(2)–C(4) | 1.501(4) |
| C(4)–C(5) | 1.488(3) | C(2)–C(3) | 1.508(2) |
| C(4)–C(6) | 1.498(3) | C(5)–C(7) | 1.492(2) |
| C(1)–C(4) | 1.525(3) | C(1)–C(1A) | 1.595(2) |
| C(1)–C(2) | 1.482(3) | C(1)–C(5) | 1.534(2) |
| C(1)–C(3) | 1.552(3) | C(1)–C(2) | 1.533(2) |
| C(5)–C(6) | 1.471(4) | C(6)–C(7) | 1.485(3) |
| C(2)–C(1)–C(4) | 108.8(2) | C(3)–C(4) | 1.499(2) |
| C(4)–C(1)–C(3) | 110.3(2) | C(5)–C(6) | 1.496(2) |
| C(2)–C(1)–C(1A) | 106.7(2) | N(1)–C(8) | 1.139(2) |
| C(3)–C(1)–C(1A) | 110.5(2) | C(8)–C(1)–C(5) | 109.3(1) |
| C(2)–C(1)–C(3) | 108.8(2) | C(8)–C(1)–C(1A) | 107.1(1) |
| C(5)–C(4)–C(1) | 121.0(2) | C(2)–C(1)–C(1A) | 111.5(1) |
| C(4)–C(1)–C(1A) | 111.7(2) | C(4)–C(2)–C(1) | 123.6(1) |
| C(6)–C(4)–C(1) | 124.8(2) | C(3)–C(2)–C(1) | 121.9(1) |
| C(1A)–C(1)–C(4)–C(6) | −88.6(3) | C(2)–C(1)–C(5) | 108.8(1) |
| C(3)–C(1)–C(4)–C(6) | 148.1(2) | C(8)–C(1)–C(2) | 108.9(1) |
| C(2)–C(1)–C(4)–C(6) | 28.9(3) | C(5)–C(1)–C(1A) | 111.2(1) |
| C(2)–C(1)–C(4)–C(5) | −42.8(3) | C(7)–C(5)–C(1) | 124.2(1) |
| | | C(6)–C(5)–C(1) | 122.3(1) |
| | | C(8)–C(1)–C(2)–C(4) | 32.8(2) |
| | | C(1)–C(2)–C(4)–C(3) | 110.3(2) |
| | | C(1)–C(5)–C(6)–C(7) | −113.7(2) |
| | | C(1A)–C(1)–C(2)–C(4) | −85.3(2) |
| | | C(5)–C(1)–C(2)–C(3) | 79.2(2) |
| | | C(2)–C(1)–C(5)–C(7) | −149.1(1) |
| | | C(1A)–C(1)–C(5)–C(6) | 160.7(1) |
| | | C(5)–C(9)–C(10)–C(4) | 151.8(1) |
| | | C(8)–C(1)–C(5)–C(6) | 42.7(2) |
| | | C(5)–C(1)–C(2)–C(4) | 151.8(1) |
| | | C(8)–C(1)–C(2)–C(3) | −39.9(2) |
| | | C(8)–C(1)–C(5)–C(7) | −30.3(2) |
| | | C(2)–C(1)–C(5)–C(6) | −76.2(2) |
| | | C(1A)–C(1)–C(5)–C(7) | 87.8(2) |

[a] Symmetry transformations: A (*meso*-**1**): $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; A (**2**): $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

## Molecular orbital calculations

We shall first examine the rotational equilibrium of the parent analogue, 1,2-dicyanoethane **4**. Experimental studies have shown that **4** exists as mixture of *trans* and *gauche* forms in condensed phases, with the latter being the lower energy form.[1,25,26] In particular, Fitzgerald and Janz have demonstrated, based on infrared spectroscopy, that pure 1,2-dicyanoethane exists entirely in the *gauche* configuration below −43.7 °C.[25] On the other hand, the *trans* rotamer was predicted to be the preferred structure in the gas phase.[1] We have calculated the *gauche*/*trans* equilibrium of 1,2-dicyanoethane in the gas phase ($\varepsilon = 1$), in a nonpolar ($\varepsilon = 2$) and a polar ($\varepsilon = 40$) medium. The *trans* rotamer is predicted to be the more stable configuration, by 4.8 kJ mol$^{-1}$, in an isolated state. The calculated *gauche*/*trans* free energy difference at 298 K ($\Delta G_{298}$) is 4.7 kJ mol$^{-1}$ (B3-LYP/6-311+G** + ZPE level). This is readily confirmed by higher-level calculations at the G3(MP2) level (3.6 kJ mol$^{-1}$). These calculated energy differences agree well with the experimental estimate of ~5 kJ mol$^{-1}$.[1] The calculated dipole moments of the *trans* and *gauche* forms are 0.0 and 18.19 × 10$^{-30}$ C m, respectively. Thus, the polar *gauche* rotamer is expected to be stabilized preferentially in a polarizable dielectric medium. Indeed, the differential solvent stabilization is sufficiently strong that the rotational equilibrium is reversed ($\Delta G_{298} = -2.7$ kJ mol$^{-1}$) even in a non-polar medium ($\varepsilon = 2$). In a polar medium of $\varepsilon = 40$, the calculated $\Delta G_{298}$ decreases further to −11.3 kJ mol$^{-1}$. Hence, our calculations confirm the observed strong preference for the *gauche* form in the liquid phase.[21] As with 1,2-dichloroethane,[20a] this change of conformational preference is attributed to solvation effects. The calculated torsional angle between the cyano groups of the *gauche* conformer is 67.1°. Introduction of a dielectric medium reduces this torsional angle significantly, by 9.2° on going from a vacuum to a dielectric medium of $\varepsilon = 40$. The calculated change in the torsional angle is in close accord with what might be expected from a solvation effect. A decrease in the CCCC torsional angle may lead to an increase in the total dipole moment of the molecule, which will provide further stabilization. It is

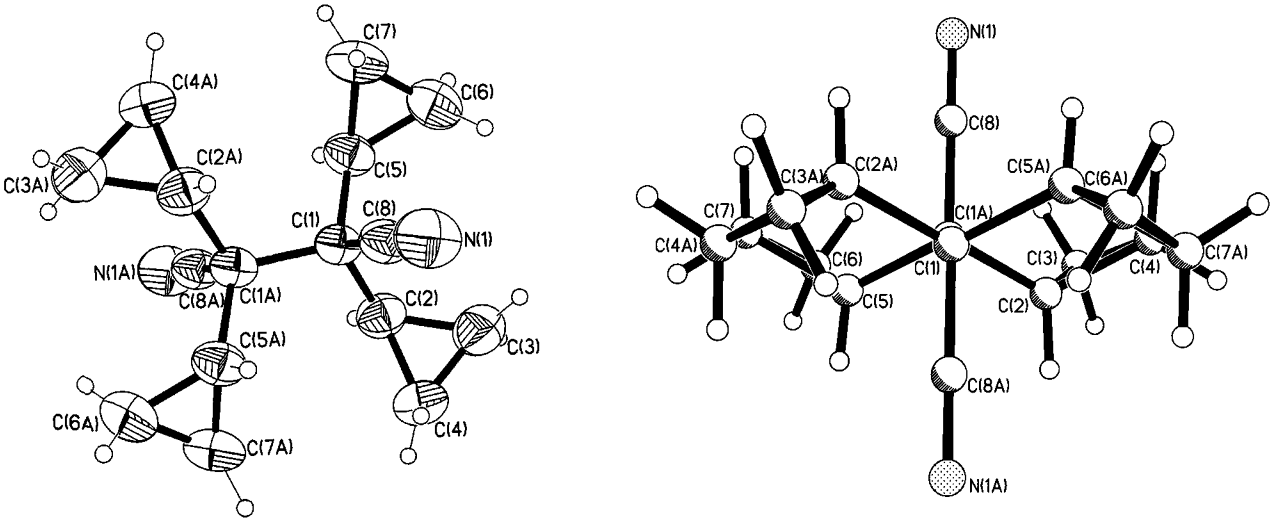

Fig. 2 Thermal ellipsoid and Newman projection diagrams of **2**.

worth noting that the calculated C–C(N) bond lengths are found to increase significantly, by 0.003 Å, in the presence of a solvent reaction field.

As with the parent analogue, the *trans* form is the preferred configuration for *meso*-**1** and (±)-**1** in the gaseous state. However, the *gauche*/*trans* energy differences are larger (Table 3). Both the *gauche* rotamers of *meso*-**1** and (±)-**1** are predicted to have similar dipole moments ($19.59 \times 10^{-30}$ and $20.59 \times 10^{-30}$ C m, respectively) to the parent compound, but the solvent stabilization energies are slightly smaller. As a consequence, the *trans* form remains the lower energy structure in a nonpolar medium. The calculated *gauche*/*trans* energies for *meso*-**1** and (±)-**1** in a dielectric medium of $\varepsilon = 2$ are in excellent accord with the experimental values in carbon tetrachloride. Furthermore, our calculations confirm the experimental finding that the *gauche*/*trans* ratio in (±)-**1** is larger than in *meso*-**1**. In a polar medium ($\varepsilon = 40$), SCRF theory predicts that the rotational equilibrium is reversed for (±)-**1**, while the *gauche*/*trans* energy difference is close to zero for *meso*-**1**.

For 1,2-dicyanotetracyclopropylethane **2**, the calculated *gauche*/*trans* energy difference in the gas phase is 3.3 kJ mol$^{-1}$, significantly smaller than those of *meso*-**1** and (±)-**1**. The calculated preference for the *trans* form is in agreement with the observed X-ray structure. In this case, the solvent stabilization of the polar *gauche* rotamer is sufficient that the rotational equilibrium is reversed, even in a nonpolar medium. This calculated result is in excellent agreement with the experimental finding that the *gauche* structure is the predominant form. Finally, we note that the calculated torsional angle between the two cyano groups is significantly smaller in *meso*-**1**, (±)-**1** and **2**, compared to the parent compound **4**. This may be attributed to the steric effect of the bulky cyclopropyl groups. The calculated geometries (B3LYP/6-31G*) of *meso*-**1**, (±)-**1**, **2** and **4** are shown in Table S1 (ESI).

**Table 3** Calculated *gauche*/*trans* energy differences ($\Delta E_0$[a] and $\Delta G_{298}$,[b] in kJ mol$^{-1}$), dipole moments[c] ($\mu$, in Debyes)[d] and torsional angles[e] ($\phi$, in degrees)

| | Gas phase ($\varepsilon = 1$) | Nonpolar medium ($\varepsilon = 2$)[f] | Polar medium ($\varepsilon = 40$)[f] |
|---|---|---|---|
| 1,2-Dicyanoethane **4** | | | |
| $\Delta E_0$ | 4.8 | −2.9 | −11.1 |
| $\Delta G_{298}$ | 4.7 | −2.7 | −11.3 |
| $\mu$ | 5.45 | 5.87 | 6.59 |
| $\phi$ | 67.1 | 63.4 | 57.9 |
| *meso*-2,3-Dicyano-2,3-dicyclopropylbutane *meso*-**1** | | | |
| $\Delta E_0$ | 10.1 | 6.2 | −0.6 |
| $\Delta G_{298}$ | 10.2 | 6.3 | −0.4 |
| $\mu$ | 5.87 | 6.29 | 6.97 |
| $\phi$ | 62.6 | 61.4 | 59.4 |
| (±)-2,3-Dicyano-2,3-dicyclopropylbutane (±)-**1** | | | |
| $\Delta E_0$ | 6.6 | 2.3 | −5.1 |
| $\Delta G_{298}$ | 5.5 | 1.2 | −6.2 |
| $\mu$ | 6.17 | 6.58 | 7.29 |
| $\phi$ | 61.7 | 60.9 | 59.6 |
| 1,2-Dicyanotetracyclopropylethane **2** | | | |
| $\Delta E_0$ | 5.0 | 0.7 | −4.2 |
| $\Delta G_{298}$ | 3.3 | −1.0 | −5.9 |
| $\mu$ | 5.76 | 6.15 | 6.86 |
| $\phi$ | 60.9 | 60.7 | 57.8 |

[a] Based on B3-LYP/6-311+G**//B3-LYP/6-31G* + ZPE level. [b] $\Delta G_{298} = \Delta H_{298} - 298\Delta S$. [c] B3-LYP/6-31G* values for the *gauche* conformers. [d] 1 D = $3.337 \times 10^{-30}$ C m. [e] Torsional angle between two cyano groups and the central C–C bond. [f] SCRF calculations: $a_0$ values for **4**, *meso*-**1**, (±)-**1** and **2** are 3.9, 5.0, 5.0 and 5.3 Å, respectively.

In summary, the rotational equilibrium in these substituted dicyanoethane systems is strongly influenced by a solvent reaction field. Hence, the preference for a particular conformer depends on the nature of the medium and the polarity of the solvent. As with 1,2-dichloroethane,[20a] the SCRF continuum model provides a useful tool to understand the solvation effects on the rotational equilibria of the compounds examined in this paper.

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