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# Molecular Conformation of Mono- and Bi-cyclic Derivatives. Part 6.[1a] Theoretical and Experimental Study of Derivatives with a Seven-membered Ring

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The electronic polarizations, dipole moments, and molar Kerr constants of cycloheptene, bicyclo[5.1.0]octane, cycloheptene oxide, and some of their oxa derivatives in carbon tetrachloride at 298 K are recorded. The conformational geometries have been studied by the molecular mechanics method. The theoretical results are compared with the experimental data in order to determine the preferred solution-state molecular conformations. The electron mobility as measured from the refractivity and polarizability exaltations is also discussed.

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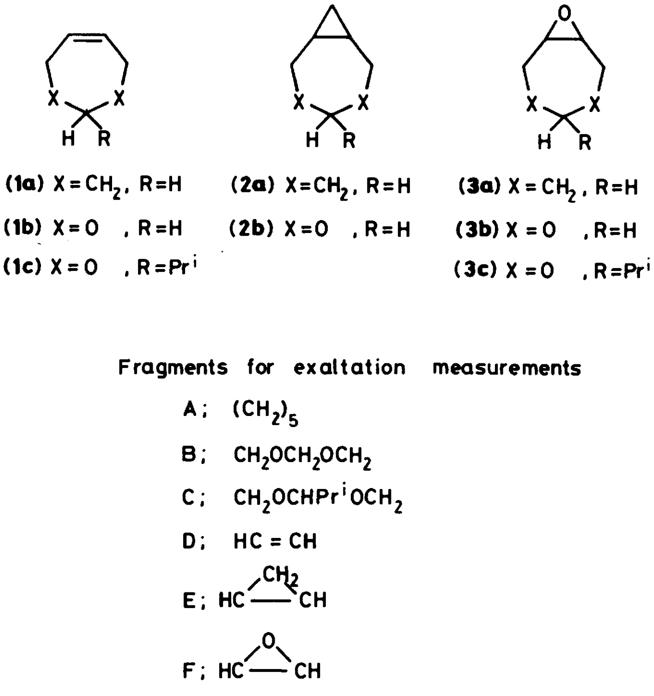
It is well known that the construction of a three-membered ring or a double bond in a cycloheptane ring reduces the conformational flexibility. N.m.r. data and conformational energy calculations indicate that cycloheptene (**1a**) prefers the chair (C) conformation. Among the possible conformations, which are the four symmetric (chair-chair, CC; boat-chair, BC; chair-boat, CB; boat-boat, BB) and the C1 form with the seven-membered ring in the twist-boat (TB) conformation, bicyclo[5.1.0]octane (**2a**) prefers the CC whereas cycloheptene oxide (**3a**) prefers the BC and C1 forms.[1b]

The introduction of oxygen atoms in place of methylene groups increases the conformational mobility of the seven-membered ring as is shown by the fact that the estimated pseudo-rotational barriers are lower for oxepane and 1,3-dioxepane than for cycloheptane.[2]

Experimental characterization of the conformational and dynamic properties of these fundamental cyclic systems is essentially based on n.m.r. and dynamic n.m.r. results. In order to gain a more quantitative understanding of these properties, we undertook a dipole moment and molar Kerr constant investigation of compounds (**1**)—(**3**).



**Scheme.**

## Experimental

*Preparation and Purification of Compounds.*—A commercial sample of cycloheptene (**1a**) was purified by distillation, b.p. 113—115 °C at $1.01 \times 10^5$ Pa, 1,3-dioxacyclohept-5-ene (**1b**), b.p. 128 °C at $1.01 \times 10^5$ Pa, and 2-isopropyl-1,3-dioxacyclohept-5-ene (**1c**), b.p. 170—171 °C at $1.01 \times 10^5$ Pa, were prepared as described in the literature.[3]

Bicyclo[5.1.0]octane (**2a**), b.p. 130 °C at $1.01 \times 10^5$ Pa, and 3,5-dioxabicyclo[5.1.0]octane (**2b**), b.p. 58 °C at 2 394 Pa, were prepared using the general procedure of LeGoff,[4] the only point of difference being the use of ammonium chloride to decompose the reaction mixture.

Cycloheptene oxide (**3a**), b.p. 160 °C at $1.01 \times 10^5$ Pa, 1,3-dioxacyclohept-5-ene oxide (**3b**), m.p. 56.5 °C, and 2-isopropyl-1,3-dioxacyclohept-5-ene oxide (**3c**) were prepared as described in the literature.[5,6] The *endo* and *exo* isomers of (**3c**) were separated by small-scale preparative g.l.c. with a stainless steel column (3 m; i.d. 5 mm) containing 5% 1,2,3-tricyanoethoxypropane on Chromosorb W (60—80 mesh) at 140 °C. Hydrogen ($3.60 \times 10^{-4}$ $m^3$ $min^{-1}$) was used as the carrier.

The purity of the compounds was checked by g.l.c. analysis with a stainless steel column (4 m; i.d. 4 mm) containing 12% SE 30 on Chromosorb G (100—120 mesh) at 150 °C. The elemental analyses were correct within experimental error. The refraction indices, i.r., and n.m.r. spectra agree with literature data; they are available upon request.

*Physical Measurements and Results.*—The densities of pure compounds were measured by a *ca.* $12 \times 10^{-6}$ $m^3$ Sprengel–Ostwald pycnometer calibrated with air-free distilled water. Details of equipment, measurements on solutions, procedure, symbols, and calculations are given elsewhere.[7]

The refractive indices, as a function of wavelength, and the density of pure liquids, as well as the incremental values of the dielectric constant, the density, the refractive index, the square of the refractive index, and the Kerr constant for the solutions in carbon tetrachloride at 298.15 ± 0.05 K are collected in Supplementary Publication No. SUP 56658 (7 pp.)*

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* For details of Supplementary Publications, see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1987, Issue 1.

**Table 1.** Molar refraction of pure compounds ($R_M$) and molar refraction at infinite dilution ($_\infty R_2$) for solutions of compounds (**1**)—(**3**) in carbon tetrachloride as a function of wavelength ($T$ 298 K)

| | | λ/nm | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | Molar refraction | 656.3 | 589.3 | 587.6 | 546.1 | 486.1 | 435.8 | 404.7 |
| (**1a**) | $R_M$ | 31.72 | 31.89 | 31.89 | 32.04 | 32.32 | 32.66 | 32.95 |
| (**1a**) | $_\infty R_2$ | 31.54 | 31.72 | 31.72 | 31.87 | 32.16 | 32.50 | 32.83 |
| (**1b**) | $_\infty R_2$ | 26.21 | 26.35 | 26.35 | 26.47 | 26.70 | 26.99 | 27.24 |
| (**1c**) | $R_M$ | 36.21 | 36.38 | 36.39 | 36.54 | 36.82 | 37.17 | 37.46 |
| (**1c**) | $_\infty R_2$ | 38.89 | 39.03 | 39.06 | 39.22 | 39.55 | 39.93 | 40.25 |
| (**2a**) | $_\infty R_2$ | 34.68 | 34.85 | 34.84 | 34.99 | 35.25 | 35.58 | 35.92 |
| (**2b**) | $_\infty R_2$ | 33.68 | 33.82 | 33.83 | 33.96 | 34.23 | 34.50 | 34.76 |
| (**3a**) | $_\infty R_2$ | 32.19 | 32.39 | 32.34 | 32.47 | 32.71 | 32.98 | 33.22 |
| (**3b**) | $_\infty R_2$ | 26.84 | 26.98 | 26.96 | 27.08 | 27.24 | 27.56 | 27.81 |
| *endo*-(**3c**) | $_\infty R_2$ | 41.07 | 41.25 | 41.25 | 41.38 | 41.69 | 42.03 | 42.36 |
| *exo*-(**3c**) | $_\infty R_2$ | 38.71 | 39.03 | 38.99 | 39.13 | 39.43 | 39.74 | 40.06 |

**Table 2.** Slopes of the least-squares fits of the dependence of dielectric constants (α), densities (β), refractive indices (γ), square of refractive indices (Γ), and Kerr constants (δ) on weight fraction for compounds (**1**)—(**3**) in carbon tetrachloride at 298 K

| Compound | α | −β | γ | Γ | δ |
|---|---|---|---|---|---|
| (**1a**) | 0.115 ± 0.003 | 0.899 ± 0.012 | 0.0062 ± 0.0002 | 0.0125 ± 0.0005 | 1.9 ± 0.1 |
| (**1b**) | 1.40 ± 0.03 | 0.460 ± 0.010 | 0.0063 ± 0.0002 | 0.0126 ± 0.0004 | −4.5 ± 1.0[a] |
| (**1c**) | 1.10 ± 0.04 | 0.632 ± 0.023 | −0.0223 ± 0.0014[a] | −0.0446 ± 0.0029[a] | −11.4 ± 0.4 |
| (**2a**) | 0.0091 ± 0.0001 | 0.817 ± 0.008 | 0.0074 ± 0.0002 | 0.0148 ± 0.0003 | 3.5 ± 0.3 |
| (**2b**) | 3.76 ± 0.04 | 0.679 ± 0.039[a] | 0.0158 ± 0.0008 | 0.0316 ± 0.0021 | −18.6 ± 0.7[a] |
| (**3a**) | 3.45 ± 0.03[a] | 0.624 ± 0.007[a] | 0.0256 ± 0.0092[a] | 0.0511 ± 0.0020[a] | −23.4 ± 1.7[a] |
| (**3b**) | 4.62 ± 0.20 | 0.262 ± 0.011 | 0.0255 ± 0.0011[a] | 0.0508 ± 0.0023[a] | −60.8 ± 1.8 |
| *endo*-(**3c**) | 1.66 ± 0.03 | 0.507 ± 0.009 | 0.0028 ± 0.0001 | 0.0055 ± 0.0002 | −32.1 ± 2.8 |
| *exo*-(**3c**) | 4.56 ± 0.08 | 0.422 ± 0.014 | 0.0040 ± 0.0002 | 0.0080 ± 0.0005 | −20.5 ± 7.9 |

[a] Non-linear regression.

**Table 3.** Experimental polarizations at infinite dilution ($_\infty P_2$), electronic polarizations ($_E P$), molar refractions ($_\infty R_2$), dipole moments (μ), and molar Kerr constants ($_m K$) of compounds (**1**)—(**3**) in carbon tetrachloride at 298 K

| Compound | $_\infty P_2$ | $_E P$ | $(_\infty R_2)_D$ | μ | $_m K$ |
|---|---|---|---|---|---|
| (**1a**)[a] | | 31.0 ± 0.0 | | | |
| (**1a**) | 36.1 ± 0.2 | 30.7 ± 0.0 | 31.7 ± 0.2 | 1.2 ± 0.1 | 3.5 ± 0.1 |
| (**1b**) | 61.1 ± 0.8 | 25.6 ± 0.0 | 26.3 ± 0.2 | 4.3 ± 0.1 | −4.5 ± 1.1 |
| (**1c**)[a] | | 35.4 ± 0.0 | | | |
| (**1c**) | 79.4 ± 1.5 | 38.0 ± 0.0 | 38.4 ± 0.6 | 4.6 ± 0.1 | −15.4 ± 0.5 |
| (**2a**) | 36.7 ± 0.2 | 33.9 ± 0.0 | 34.8 ± 0.2 | 0.3 ± 0.2 | 5.8 ± 0.4 |
| (**2b**) | 136.4 ± 1.2 | 33.0 ± 0.0 | 33.8 ± 0.6 | 7.4 ± 0.1 | −23.7 ± 0.8 |
| (**3a**) | 124.7 ± 0.9 | 31.6 ± 0.0 | 32.7 ± 0.1 | 7.0 ± 0.0 | −28.3 ± 1.9 |
| (**3b**) | 153.5 ± 5.5 | 26.2 ± 0.0 | 26.6 ± 0.2 | 8.3 ± 0.2 | −74.4 ± 2.1 |
| *endo*-(**3c**) | 105.6 ± 1.1 | 40.3 ± 0.0 | 41.2 ± 0.3 | 5.8 ± 0.1 | −51.0 ± 4.3 |
| *exo*-(**3c**) | 211.3 ± 3.0 | 38.0 ± 0.0 | 39.0 ± 0.4 | 9.6 ± 0.1 | −37.6 ± 12.5 |

[a] From measurements on the pure substance.

Table 1 reports the molecular refractions obtained from the measurement of the refractive indices on the pure compounds, $R_M$, and at infinite dilution, $_\infty R_2$, for solutions in $CCl_4$, as a function of the wavelength. Tables 2 and 3 show polarizations, refractions, dipole moments, and molar Kerr constants calculated from the values in Table 1. All these quantities are given throughout in SI units; $R_M$ (or $_E P$) $10^{-6}$ m$^3$, $b$ $10^{-40}$ C m$^2$ V$^{-1}$, μ $10^{-30}$ C m, and $_m K$ $10^{-27}$ m$^5$ V$^{-2}$ mol$^{-1}$. All errors are quoted as standard deviations.

## Calculations and Results

Theoretical dipole moments and molar Kerr constants were calculated as previously reported.[7] A modified version of the empirical force field method of Schleyer *et al.*[8] was used by adopting the pattern search minimization technique. Details of calculations on molecules (**1a**), (**2a**), (**2b**), (**3a**), and (**3b**) have been previously reported.[1b,9] For molecules (**1b** and **c**), the calculations were carried out by considering the boat (B, $C_s$ symmetry), the chair (C, $C_s$ symmetry) and the twist-boat (TB, $C_1$ symmetry) forms (Figure 1). For compound (**3c**), only the twist-boat ($C_1$ symmetry) and the boat-chair (BC, $C_s$ symmetry) forms were considered (Figure 2). Geometrical parameters calculated for the most stable conformations of the molecules (**1b**), (**1c**), *endo*-(**3c**), and *exo*-(**3c**) are given in Tables 4—6.

The calculated strain energies ($E_s$) together with the dipole moments and molar Kerr constants for the most stable conformations of all the compounds are given in Table 7 and compared with experimental data.

All the calculations were carried out on a Siemens VM/370 computer at SIAM, Milan.

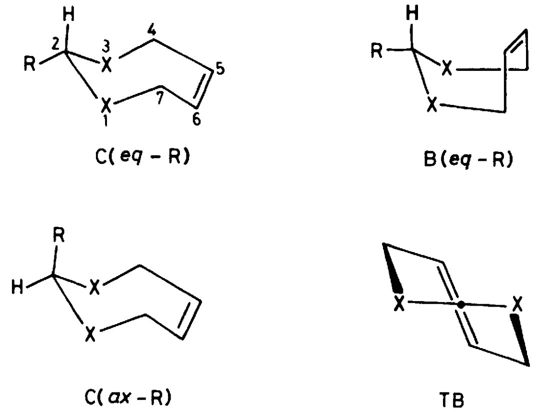

Figure 1. 1,3-Dioxacyclohept-5-ene forms

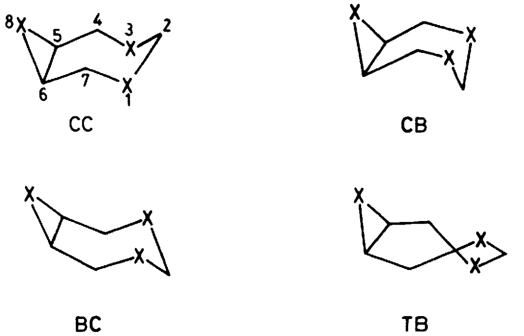

Figure 2. 1,3-Dioxacyclohept-5-ene oxide forms

**Table 4.** Geometrical parameters of 1,3-dioxacyclohept-5-ene (**1b**)

| | C | B | TB |
|---|---|---|---|
| Bond length (pm) | | | |
| C(5)–C(6) | 133.3 | 133.4 | 133.6 |
| C(4)–C(5) | 150.7 | 150.1 | 150.8; 150.7 |
| O(3)–C(4) | 141.0 | 141.3 | 141.1; 141.1 |
| O(1)–C(2) | 140.8 | 141.0 | 140.6; 140.6 |
| C(5)–H | 109.5 | 109.5 | 109.6; 109.6 |
| $C_n$–H[a] | 110.4 | 110.4 | 110.4 |
| Bond angle (rad)[b] | | | |
| O(3)C(4)C(5) | 1.941 | 1.974 | 1.965; 1.950 |
| C(2)O(3)C(4) | 2.019 | 2.025 | 1.988; 1.984 |
| O(1)C(2)O(3) | 1.990 | 1.981 | 1.958 |
| C(4)C(5)C(6) | 2.098 | 2.086 | 2.159; 2.138 |
| C(6)C(5)H | 2.100 | 2.108 | 2.073; 2.084 |
| $HC_nH$[a] | 1.873 | 1.841 | 1.908 |
| Dihedral angle (rad) | | | |
| $\beta$ | 2.128 | 2.154 | |
| $\gamma$ | 2.135 | 2.166 | |
| $\omega_{45}$ | −1.110 | −1.110 | −0.644; −0.717 |
| $\omega_{34}$ | 1.440 | 0.385 | 1.518; 1.560 |
| $\omega_{23}$ | −1.176 | 1.141 | −0.848; −0.805 |
| $\omega_{56}$ | 0.0 | −0.005 | 0.106 |

[a] Averaged value. [b] 1 rad = 180/π°.

**Table 5.** Geometrical parameters of 2-isopropyl-1,3-dioxacyclohept-5-ene (**1c**)

| | ax-Pr$^i$ | eq-Pr$^i$ | | |
|---|---|---|---|---|
| | C | C | B | TB |
| Bond length (pm) | | | | |
| C(5)–C(6) | 133.2 | 133.2 | 133.4 | 133.6 |
| C(4)–C(5) | 150.4 | 150.3 | 149.9 | 150.5; 150.5 |
| O(3)–C(4) | 140.7 | 140.8 | 141.2 | 141.0; 140.9 |
| O(1)–C(2) | 140.9 | 140.3 | 140.5 | 140.0; 140.5 |
| C(2)–C | 152.7 | 153.3 | 153.0 | 153.0 |
| C–C (Pr$^i$) | 153.4 | 153.3 | 153.3 | 153.4; 153.3 |
| C(5)–H | 109.5 | 109.5 | 109.5 | 109.6; 109.6 |
| $C_n$–H[a] | 110.4 | 110.3 | 110.3 | 110.3 |
| Bond angle (rad) | | | | |
| O(3)C(4)C(5) | 1.904 | 1.909 | 1.974 | 1.972; 2.035 |
| C(2)O(3)C(4) | 2.047 | 2.061 | 2.051 | 2.023; 1.995 |
| O(1)C(2)O(3) | 2.053 | 2.012 | 1.958 | 1.960 |
| C(4)C(5)C(6) | 2.079 | 2.080 | 2.084 | 2.161; 2.150 |
| O(1)C(2)C | 1.995 | 1.859 | 1.892 | 1.983; 1.923 |
| C(6)C(5)H | 2.110 | 2.108 | 2.108 | 2.072; 2.079 |
| $HC_nH$[a] | 1.841 | 1.848 | 1.841 | 1.909 |
| Dihedral angle (rad) | | | | |
| $\beta$ | 2.049 | 2.061 | 2.159 | |
| $\gamma$ | 2.307 | 2.292 | 2.196 | |
| $\omega_{45}$ | 1.203 | 1.178 | −1.101 | −0.656; −0.716 |
| $\omega_{34}$ | −1.417 | −1.435 | 0.374 | 1.478; 1.555 |
| $\omega_{23}$ | 0.983 | 1.025 | 1.122 | −0.791; −0.846 |
| $\omega_{56}$ | 0.002 | 0.0 | −0.002 | 0.136 |
| $\omega$ (Pr$^i$) | ±0.848 | ±0.955 | ±0.981 | −1.040; 0.864 |

[a] Averaged value.

## Discussion

The dipole moments calculated for the three possible conformers of the cycloheptene (**1a**) are nearly equal and are greater than the experimental value. On the other hand, the experimental value of the molar Kerr constant in carbon tetrachloride at 25 °C (Table 7) is in agreement with that calculated for the C form: in solution, this form should be preferred.

Molecular mechanics calculations indicate that the TB conformation is the most stable for compound 1,3-dioxacyclohept-5-ene (**1b**). The dipole moment and the molar Kerr constant values in carbon tetrachloride can be regarded as average values connected with the dipole moments and the molar Kerr constants of the individual forms by the relations: $\mu^2 = \Sigma_i x_i \cdot \mu^2$ and ${}_{\mathrm{m}}K = \Sigma_i x_i \cdot {}_{\mathrm{m}}K_i$ where $x_i$ is the molar fraction of the $i$th conformer. By considering a TB $\rightleftharpoons$ C equilibrium in solution, the following compositions may be obtained from the values reported in Table 7: 51% (TB)–49% (C) from μ values and 91% (TB)–9% (C) from ${}_{\mathrm{m}}K$ values. The latter composition is consistent with n.m.r. measurements which give the TB form as preferred when the substituents in position 2 are both hydrogen atoms or are equal.

For 2-isopropyl-1,3-dioxacyclohept-5-ene (**1c**), force field calculations give the TB form as the most stable; in the C form, the isopropyl group should prefer the equatorial position. An equilibrium composition of 40% (TB)–60% (C) may be estimated from μ values while a 80% (TB)–20% (C) composition is estimated from ${}_{\mathrm{m}}K$ values.

The dipole moments calculated for the four possible forms of bicyclo[5.1.0]octane (**2a**) (the BB form being energetically unfavoured and therefore not considered)[1b] are nearly equal; so, they are not useful for the conformational analysis. The calculated molar Kerr constants are all lower than the experimental one but the closest to the experimental value is that for the CC form. The CC conformation appears to be the most stable both from molecular mechanics and quantum-mechanical calculations (MINDO/3).[1b]

**Table 6.** Geometrical parameters of 2-isopropyl-1,3-dioxacyclohept-5-ene oxides *endo*- and *exo*- (**3c**)

| | *endo* | | *exo* |
|---|---|---|---|
| | BC | TB | TB |
| Bond length (pm) | | | |
| C(5)–C(6) | 147.2 | 147.4 | 147.2 |
| C(4)–C(5) | 151.8 | 152.6; 152.2 | 152.7; 153.0 |
| C(5)–O(8) | 143.6 | 143.7; 143.6 | 143.7; 143.7 |
| C(4)–O(3) | 140.0 | 140.7; 140.4 | 140.9; 140.7 |
| O(1)–C(2) | 139.7 | 140.1; 140.3 | 140.1; 140.5 |
| C(2)–C | 153.4 | 153.1 | 153.3 |
| C–C (Pr$^i$) | 153.4 | 153.2; 153.7 | 153.8; 153.3 |
| C(5)–H | 110.4 | 110.4; 110.4 | 110.3; 110.3 |
| $C_n$–H$^a$ | 110.2 | 110.2 | 110.2 |
| Bond angle (rad) | | | |
| O(3)C(4)C(5) | 2.054 | 1.950; 2.021 | 1.923; 2.044 |
| C(2)O(3)C(4) | 2.033 | 2.000; 2.011 | 1.979; 1.998 |
| O(1)C(2)O(3) | 1.897 | 1.925 | 1.929 |
| C(5)C(6)C(7) | 2.117 | 2.096; 2.080 | 2.098; 2.079 |
| C(5)C(6)O(8) | 1.033 | 1.031; 1.031 | 1.033; 1.033; |
| C(5)O(8)C(6) | 1.075 | 1.079 | 1.075 |
| O(1)C(2)C | 1.871 | 2.016; 1.881 | 1.929; 2.026 |
| C(2)CC | 1.974 | 2.004; 1.913 | 1.904; 1.963 |
| C(5)C(6)H | 2.011 | 2.056; 2.021 | 2.046; 2.025 |
| H$C_n$H$^a$ | 1.861 | 1.847 | 1.852 |
| Dihedral angle (rad) | | | |
| $\alpha$ | 1.890 | | |
| $\beta$ | 2.409 | | |
| $\gamma$ | 1.977 | | |
| $\omega_{45}$ | 0.813 | −0.799; −0.623 | −0.768; −0.609 |
| $\omega_{34}$ | −1.346 | 1.662; 1.538 | 1.716; 1.494 |
| $\omega_{12}$ | 1.407 | −0.813; −0.876 | −0.908; −0.791 |
| $\omega_{56}$ | 0.0 | 0.140 | 0.099 |
| $\omega_{58}$ | 1.934 | 1.946; −1.911 | 1.929; −1.915 |
| $\omega$ (Pr$^i$) | ±1.004 | 0.780; −1.131 | −1.040; 0.855 |

[a] Averaged value.

Molecular mechanics calculations[1b] indicate that the TB form is the most stable for 3,5-dioxabicyclo[5.1.0]octane (**2b**). However, the experimental dipole moment and the molar Kerr constant values support the existence of an equilibrium BC $\rightleftharpoons$ CC; these results agree with the analysis of the coupling constants measured for the 4-isopropyl derivatives which is consistent with a chair conformation of the seven-membered ring, *i.e.* CC for the *exo*-isomer and BC for the *endo*-isomer.[6]

In cycloheptene oxide (**3a**), a similar strain energy was found for the TB, BC, and CC conformers whereas that of the CB form is higher. The calculated dipole moments are practically independent of the conformation; moreover, all the calculated values are similar to the experimental one. On the other hand, the theoretical molar Kerr constants are strongly dependent on the molecular conformations. Electron-diffraction studies indicate a BC $\rightleftharpoons$ CC equilibrium in the gaseous phase with a ratio 66% (BC)–34% (CC). From this equilibrium composition, $_mK$ −31.9 can be calculated, in good agreement with the experimental value (−28.3). If the equilibrium composition in the solution is evaluated from the strain energies, the calculated value of the molar Kerr constant is −48.2. Both this result and the preceding observations about compound (**2b**) seem to indicate that the energy values for the TB form are under-estimated in our force field program probably owing to an inadequate calculation of the electrostatic interactions between the heteroatoms.

**Table 7.** Theoretical strain energies ($E_s$), dipole moments ($\mu$), and molar Kerr constants ($_mK$) for compounds (**1**)—(**3**)

| Compound | Form | $E_s$$^a$ | $\mu$ | $_mK$ |
|---|---|---|---|---|
| (**1a**) | exp. | | 1.2 ± 0.1 | 3.5 ± 0.1 |
| | TB | 48.15 | 1.6 | 4.5 |
| | C | 46.47 | 1.7 | 3.3 |
| | B | 59.87 | 1.7 | 0.37 |
| (**1b**) | exp. | | 4.3 ± 0.1 | −4.5 ± 1.1 |
| | TB | 98.39 | 0.48 | 3.0 |
| | C | 111.79 | 6.1 | −83.7 |
| | B | 130.63 | 4.2 | −0.95 |
| (**1c**) | exp. | | 4.6 ± 0.1 | −15.4 ± 0.5 |
| | TB | 91.27 | 0.32 | 4.0 |
| | C(*eq*-Pr$^i$) | 108.02 | 5.8 | −87.6 |
| | C(*ax*-Pr$^i$) | 115.56 | 5.6 | −85.7 |
| | B(*eq*-Pr$^i$) | 120.16 | 4.1 | 4.8 |
| (**2a**) | exp. | | 0.3 ± 0.2 | 5.8 ± 0.4 |
| | TB | 169.98 | 0.59 | 0.76 |
| | CC | 155.33 | 0.46 | 2.4 |
| | CB | 164.12 | 0.62 | 1.6 |
| | BC | 174.17 | 0.57 | 0.57 |
| (**2b**) | exp. | | 7.4 ± 0.1 | −23.7 ± 0.8 |
| | TB | 214.78 | 0.10 | 0.42 |
| | CC | 226.09 | 6.4 | −22.7 |
| | CB | 229.44 | 5.1 | 18.6 |
| | BC | 226.51 | 6.5 | −28.6 |
| (**3a**) | exp. | | 7.0 ± 0.0 | −28.3 ± 1.9 |
| | TB | 193.43 | 6.6 | −37.9 |
| | CC | 197.20 | 6.7 | −8.0 |
| | CB | 210.60 | | |
| | BC | 194.69 | 6.5 | −78.3 |
| (**3b**) | exp. | | 8.3 ± 0.2 | −74.4 ± 2.1 |
| | TB | 241.58 | 3.9 | −11.9 |
| | CC | 258.74 | | |
| | CB | 270.89 | | |
| | BC | 247.86 | 10.6 | −161 |
| *endo*-(**3c**) | exp. | | 5.8 ± 0.1 | −51.0 ± 4.3 |
| | TB | 229.44 | 6.2 | −74.6 |
| | BC | 239.07 | 12.3 | −359 |
| *exo*-(**3c**) | exp. | | 9.6 ± 0.1 | −37.6 ± 12.5 |
| | TB | 229.44 | 6.0 | −36.1 |

[a] In kJ mol$^{-1}$.

The experimental dipole moment and molar Kerr constant of 1,3-dioxacyclohept-5-ene oxide (**3b**) can be interpreted by considering a TB $\rightleftharpoons$ BC equilibrium with a ratio 1:1 of the two conformers. In the crystalline state, the molecule has the BC conformation and the experimental geometrical parameters agree with the calculated ones.[1b] The dynamic n.m.r. spectrum suggests that the molecule might be in a TB conformation even allowing for the existence of an equilibrium TB $\rightleftharpoons$ BC with a low energy barrier.[6]

The preferred conformation of the *endo* and *exo* isomers of 2-isopropyl-1,3-dioxacyclohept-5-ene oxide (**3c**) is the TB form.[6] For this form, the theoretical dipole moment and molar Kerr constant are in agreement with the experimental values. Moreover, supporting evidence for the prevalence of the TB conformation has been inferred from the values of the coupling constants.

In previous papers[10,11] it was shown that the refractivity and polarizability exaltations may be used to estimate the increased electron mobility in conjugated and hyperconjugated systems. Of course, a good knowledge of atoms, groups, and/or bond properties is needed to obtain reliable estimates.

In this view, each of the molecules (**1**)—(**3**) was built up from fragments and experimental $(_\infty R_2)_D$ and $_EP$ data (Table 3) were used to estimate 'fragment' refractions and polarizations. By imposing the previously calculated parameters for the

**Table 8.** Molar refractions and electronic polarizations of the fragments

| | Molar refractions | | | | Electron polarizations | |
|---|---|---|---|---|---|---|
| Method | 1[a] | 2[b] | 3[c] | 4[d] | 1[a] | 3[c] |
| Fragment | | | | | | |
| A | 22.5 ± 0.8 | 23.2 | 21.9 | 22.6 ± 0.9 | 21.3 ± 1.0 | 21.5 |
| B | 16.2 ± 1.0 | 17.4 | 16.2 | 16.8 ± 0.9 | 15.9 ± 0.9 | 15.8 |
| C | 30.1 ± 1.0 | 31.4 | 30.2 | 30.8 ± 0.9 | 29.5 ± 0.9 | 29.5 |
| D | 9.2 ± 0.8 | 8.8 | 10.1 | 9.5 ± 0.9 | 9.1 ± 0.2 | 9.7 |
| E | 13.8 ± 0.0 | 13.6 | 13.8 | 13.7 ± 0.0 | 13.4 ± 0.0 | 13.4 |
| F | 10.2 ± 0.0 | 10.2 | 10.2 | 10.2 ± 0.0 | 10.0 ± 0.0 | 10.0 |

[a] From experimental values of $({}_{\infty}R_2)$ and ${}_{E}P$ (Table 3). [b] From atom and group contributions (ref. 13). [c] From bond contributions (ref. 13). [d] Mean values from methods 2 and 3.

cyclopropane[1] and for the oxirane[12] residues, the solutions of the equation's systems furnish the results reported in Table 8. For the sake of comparison, the molar refractions and the electronic polarizations calculated from atom and group contributions[13] as well as from bond contributions[13] are reported in the same Table. It can be seen that the 'fragment' values obtained from the experimental refractions and polarizations of molecules (**1**)—(**3**) are in quite good agreement with the mean values obtained from literature data.

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