Tetrahedron. Vol 33, pp. 57 to 64 Pergamon Press 1977 Printed in Great Britain

STERIC EFFECTS IN 5-MEMBERED RINGS—VIII

A CONFORMATIONAL ANALYTICAL STUDY OF *CIS*- AND *TRANS*-1,3-DICHLOROCYCLOPENTANE

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(*Received UK* 24 *February* 1976; *Accepted for publication* 29 *June* 1976)

Abstract—A study of the title systems was performed using theoretical calculations, dipole moments (experimental and calculated) and NMR spectroscopy. The results were discussed in the light of literature data on related systems. It was concluded that a multitude of conformations occur in a potential well for the *cis*-isomer and that for the *trans*-one, an even flatter and more variegated distribution in a double minimum is indicated.

The intricacy of cyclopentane conformational analysis is, by now, well documented,[2,3] the main cause being the (pseudorotational) mobility of the system.[2-4]

Our investigations have been concentrated on cyclopentanes, substituted in 1,3-positions, the rationale of the choice being that, as pseudorotation is necessarily inhibited, one can scrutinize the ring without spurious steric interference between the substituents. In this framework we have looked into physical and chemical properties of various derivatives,[5a,c] CrO$_3$ oxidation kinetics of suitably substituted alcohols[1,5b,c] and relative stabilities of stereoisomers.[5a-d] However, these approaches, which had been used with considerable success in the conformational analysis of 6-membered rings, have led, in the case of the 5-membered ring, to results which lent themselves to frustratingly qualitative interpretation. Such was, in fact, also the fate of many 5-membered ring investigations from other laboratories, and this led sometimes to regrettable oversimplifications.[2] It gradually became clear[1-5] that this behavior stems from the fact that 5-membered ring compounds do not necessarily occur in well-defined, single symmetric conformations (except in crystals) but rather in a multitude of intermediate ones. Direct proof for this assertion was still to be provided.

We present here a combined effort, using dipole moment measurements and calculation, NMR spectroscopy and energy calculations, to look into the conformation of the stereoisomeric 1,3-dichlorocyclopentanes.

For the purpose of this investigation, we prepared *cis*- and *trans*-1,3-dichlorocyclopentane and their respective 1,3-dideutero derivatives from *cis*- and *trans*-cyclopentane-1,3-dicarboxylic acid respectively, using the Hunsdiecker method. The dichlorides were identical to those obtained by chlorination of cyclopentyl chloride[6] and the original stereochemical assignments were thus confirmed.

The electrical dipole moments of the 1,3-dichlorocyclopentanes (as well as those of the corresponding 1,3-dicarbonitriles[5d]) were determined and are listed in Table 1.

As expected, the dinitriles with their greater group moments (*vide infra*), exhibited larger dipole moments and more pronounced solvent dependence.

The next step was to calculate theoretical dipole moments for comparison with the experimental values. There we already encounter the difficulty inherent to the flexible 5-membered ring, viz. there are no *a priori* known preferred conformations and an infinity of possible geometries should be assumed. This was obviated as usual[3,4] by considering only those forms where the basic ring is of C$_s$ (envelope) or C$_2$ (half-chair) symmetry,[4] but keeping in mind that the true conformations may well be neither of them but rather intermediate ones. The complete pseudorotation circuits of *cis* and *trans*-1,3-disubstituted cyclopentane are depicted below (Figs. 1 and 2, respectively).

There are five half-chairs and six envelopes with *cis* configuration and six half-chairs and five envelopes of *trans* configuration to be considered. All these were included in the calculation of the theoretical dipole moments, using unit substituent vectors. The envelope (E) and half-chair (H) ring geometries as expressed by their atomic coordinates were taken from a calculation by Lugar[7] and the substituents were added in the appropriate positions (*vide infra*). The partial moments that we used were 3.74 D for C–CN which is the experimental value for cyanocyclopentane[8a] and 2.05 D for C–Cl which is the average experimental value for chlorocyclopentane in benzene and tetrachloromethane[8b] (at 25°). The theoretical dipole moment of every conformer were then determined by addition of the appropriate unit vectors and by multiplying the resulting vector by the corresponding partial moment.† The results of these calculations are listed in Table 2. For ready reference we depicted the basic conformations (E and H) in Fig. 3.

We turn now to energy calculations. These were performed on all conformers of *cis*- and *trans*-

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†A major concern in these calculations were the induction effect, viz. induction in the ring and mutual induction of the polar substituents.[9-14] Inclusion of those in our calculation, although possible, would complicate matters considerably, due to the multitude of conformations involved. In addition to that, and in contrast to the situation in 6-membered rings,[11-13] there are not only well-defined axial and equatorial C–X bonds to be considered, but such of intermediate geometry for which the evaluation of, e.g. ring induction effects would be quite hazardous and qualitative at best.

Fortunately, it appears to be possible to obviate this difficulty, since in our cases with two relatively distant (1, 3) dipoles, the mutual induction should contribute very little and ring induction by each polar substituent should undergo, at least in part, mutual concellation, especially since we took chlorocyclopentane as the basis for the C–Cl partial moment. THis line of reasoning led us to neglect induction effects in our calculations. This was supported by the finding that in m-dichlorobenzene, in contrast to the *ortho* isomer, induction effect add very little to the originally calculated value[10] and in hexachlorocyclohexanes, correct values are achieved by inclusion of only *vicinally* induced moments.[11]

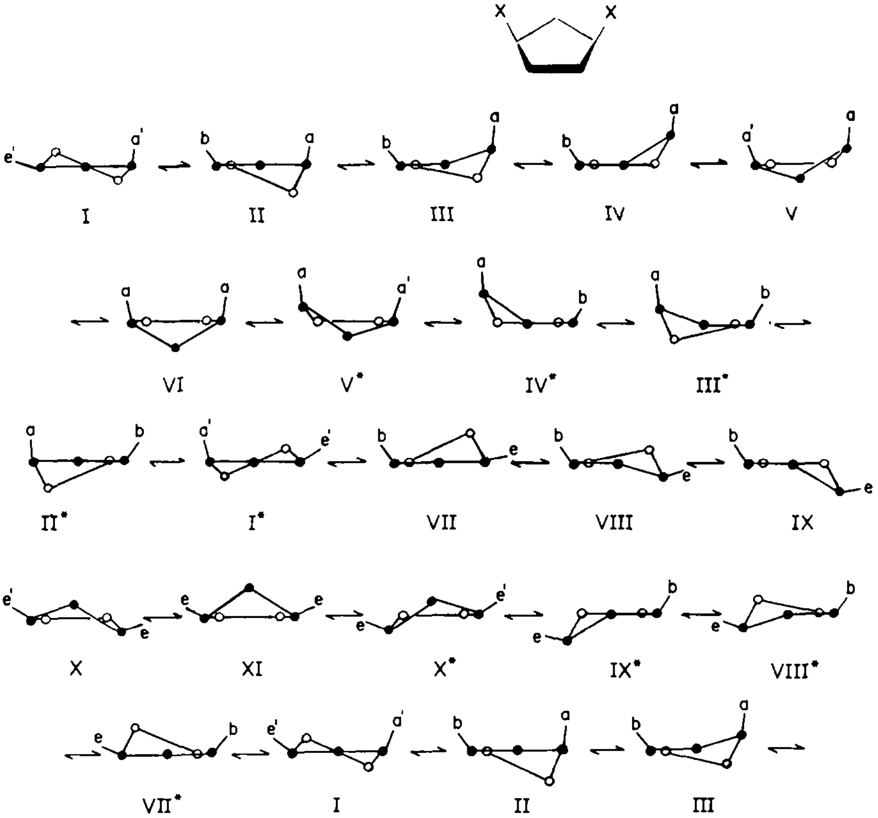

Fig. 1. Complete pseudorotation circuit for *cis*-1,3-dichlorocyclopentane: five half-chair (enantiomeric pairs) and six envelope (four of them as enantiomeric pairs) conformations: a = axial; e = equatorial; a′ = quasi-axial; e′ = quasi-equatorial; b = bisectional.

Table 1. Experimental dipole moments (D at 25°C)

Cyclopentane	*cis*	*trans*	Solvent
1,3-Dichloro-	2.73	1.44	Tetrachloromethane
	2.76	1.44	Benzene
1,3-Dicyano-	4.51	2.78	Tetrachloromethane
	4.70	2.87	Benzene
	4.70	2.87	Dioxane

dichlorocyclopentane, taking into account torsional strain, non-bonded interactions and electrostatic (dipole–dipole) interactions. Lugar had calculated minimum energy conformations of cyclopentane (E and H) from (H–H) non-bonded interactions, bond bending energy (using a composite function with a quadratic term for small angle changes and a linear term for large changes) and bond torsion energy (using the standard three-fold cosine function.[7]

In Table 3 we list the atomic coordinates of E and H, as

Table 2. Calculated dipole moments of stereoisomeric 1,3-dicyano- and -dichlorocyclopentanes (in Debye units)

cis-Stereoisomers				*trans*-Stereoisomers			
Conformation[(a)]	(b)	Dinitrile	Dichloride	Conformation	(c)	Dinitrile	Dichloride
E(2d–5d)	VI	7.45	4.09	E(2d–5u)	VI	3.79	2.08
H(3u–5u)	V	7.43	4.07	H(2d–4u)	V	3.76	2.06
E(1u–3u)	IV	7.28	3.99	H(2u–4d)	VII	3.57	1.96
H(1u–3u)	III	7.07	3.88	E(1d–3u)	IV	3.31	1.82
E(2d–4d)	II	6.69	3.67	H(1u–3d)	III	3.06	1.68
H(2u–5u)	I	6.08	3.33	E(1u–3d)	VIII	2.80*	1.54
E(2u–4u)	VII	5.41	2.97	E(2u–4d)	II	2.56	1.40*
H(1d–3d)	VIII	4.86	2.66*	H(2u–5d)	I	2.28	1.25
E(1d–3d)	IX	4.53*	2.48	H(1d–3u)	IX	2.14	1.17
H(3d–5d)	X	3.98	2.18	E(2d–4u)	X	1.17	0.64
E(5u–5u)	XI	3.84	2.10	H(2d–5u)	XI	0.33	0.18

(a) d = down; u = up.[b,c]
(b) see Fig. 1.
(c) see Fig. 2.
* the asterisks indicate the corresponding location of the experimental values (see Table 1).

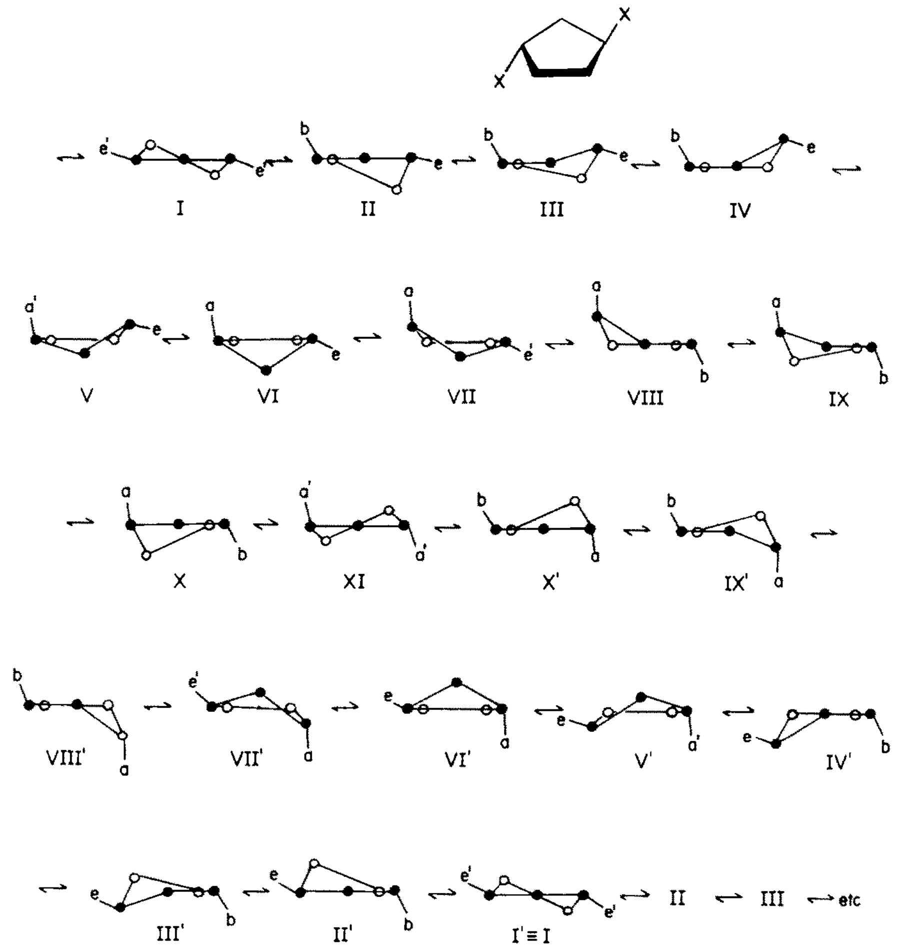

Fig. 2. Complete pseudorotation circuit for *trans*-1,3-dichlorocyclopentane: six half-chair and five envelope conformations (see also caption of Fig. 1).

Table 3. Atomic coordinates expressed in Angstrom units, of the envelope (E) and half-chair (H) minimum energy conformers of cyclopentane, according to Lugar[7]

	Envelope (E) conformation			Half-chair (H) conformation		
Atom[(a)]	x	y	z	x	y	z
C1	0.000	0.000	0.297	0.000	0.000	0.000
C2	0.867	1.138	−0.241	0.954	1.180	−0.182
C3	2.311	0.764	0.092	2.326	0.705	0.295
C4	2.311	−0.764	0.092	2.326	−0.705	−0.295
C5	0.867	−1.138	−0.241	0.954	−1.180	0.182
H1u	−0.028	0.000	1.401	−0.621	0.139	0.902
H1d	−1.001	0.000	−0.168	−0.621	−0.139	−0.902
H2u	0.597	2.086	0.257	0.617	2.035	0.429
H2d	0.741	1.225	−1.334	1.003	1.465	−1.248
H3u	2.587	1.148	1.089	2.373	0.673	1.397
H3d	2.995	1.148	−0.685	3.132	1.318	−0.144
H4u	2.587	−1.148	1.089	3.132	−1.318	0.144
H4d	2.995	−1.148	−0.685	2.373	−0.673	−1.397
H5u	0.597	−2.086	0.257	1.003	−1.465	1.248
H5d	0.741	−1.225	−1.334	0.617	−2.035	−0.429

(a)see Figs. 3 and 4; u = up; d = down.

determined by Lugar[7] and Fig. 3 shows their location in an appropriate Cartesian coordinate system. Using next techniques of vector analysis and taking a bond-length value of 1.80 Å for C–Cl[17] the latter were added to the basic frameworks and the atomic coordinates of chlorine atoms in all possible locations are listed in Table 4. The various isomeric dichlorocyclopentanes could then be constructed from the coordinates in Table 3 and picking out the desired Cl coordinates from Table 4.

Since the minimum energy envelope and half-chair of

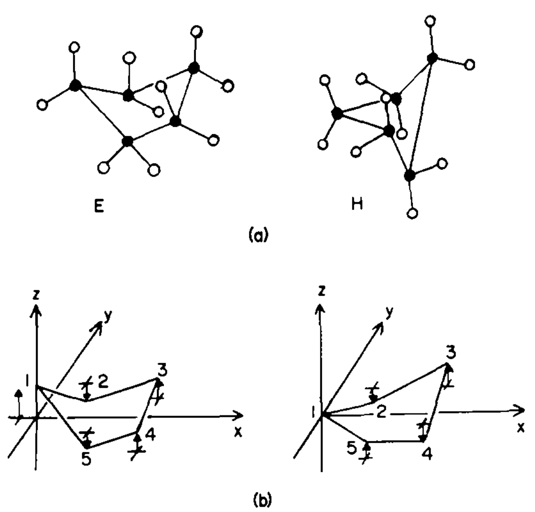

Fig. 3. The two basic symmetric conformations of cyclopentane: E = envelope (C_s); H = half-chair (C_2); black circles—carbon atoms, white circles—hydrogen atoms. The lower part shows them in a Cartesian coordinate system, with vertical displacements of the ring atoms.

cyclopentane have been calculated with recent force fields to be virtually isoenergetic[7,18,19] and since a full molecular mechanics calculation with energy minimization was beyond the scope of this work we approached the problem by evaluating the energy differences obtained by introducing the polar substituents onto the basic frames.† To this end, we used: (a) a torsional term $E_t = \Delta V^\circ/2\Sigma(1 + \cos 3\psi)$, where ΔV° is the difference between the torsional barrier for chloroethane and that for ethane (3.680 and 2.875 kcal/mol respectively[20]), the summation being over all the C–C bonds adjacent to C–Cl; (b) a term for non-bonded interactions which is essentially the Hill expression[21]: $E_{nb} = -2.25\epsilon(r^*/r)^6 + 8.28 \times 10^5\,\epsilon \exp(-r/0.0736\,r^*)$ where r is the interatomic distance, r* the sum of the Van der Waals radii and ϵ a scaling factor for every element and their values were taken from the literature;[7,21,22] (c) a term for electrostatic (dipole–dipole) interactions[23] $E_{\mu\mu} = [(\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2) - 3(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})/r^2]/r^3D$, where $r = |\mathbf{r}|$, $\mathbf{r}$ being the vector joining the point dipoles. The latter are supposedly located at a certain distance along the C–Cl bond and two values can be found in the literature, one at 7/8 of the C–Cl bond length[24] and the second at 0.77 Å form C.[25] Another source of difficulties is the dielectric constant D for which values of 1–4 have been considered.[26,27] Calculations with both r values and D = 1 or 2.24 (CCl_4) were performed and, surprisingly, the *end-results* varied very little. We present (Table 5) therefore, one set of results with r = 1.57 Å and D = 1 but refer to the others (see Table 5 and below).

In Table 5 we listed the calculated torsional, non-bonded electrostatic and total energy differences, relative to the most stable conformer in each series; along with the molar distribution of the conformers in each series as calculated by the simplified Maxwell–Boltzmann function $X_n/X_0 = \exp(-\Delta E/RT)$, including a probability factor of 2 for all dissymmetric conformations. The energy profiles for the pseudorotational circuit of the *cis*- and *trans*-compound under scrutiny are given in Figs. 5 and 6 respectively.

In the last columns of Table 5, the theoretical dipole moments are given, as calculated from the data of Table 2 and the conformational distribution derived above (μ_1 was calculated using X in Table 5, the others were obtained using the other distributions using the remaining r and D combinations). Considering the approximations involved, the agreement is good for the *cis*-compound although less so for the *trans*-isomer.

Finally, an NMR spectroscopical study was undertaken, with the aim of analysing the CH_2–CH_2 pattern and

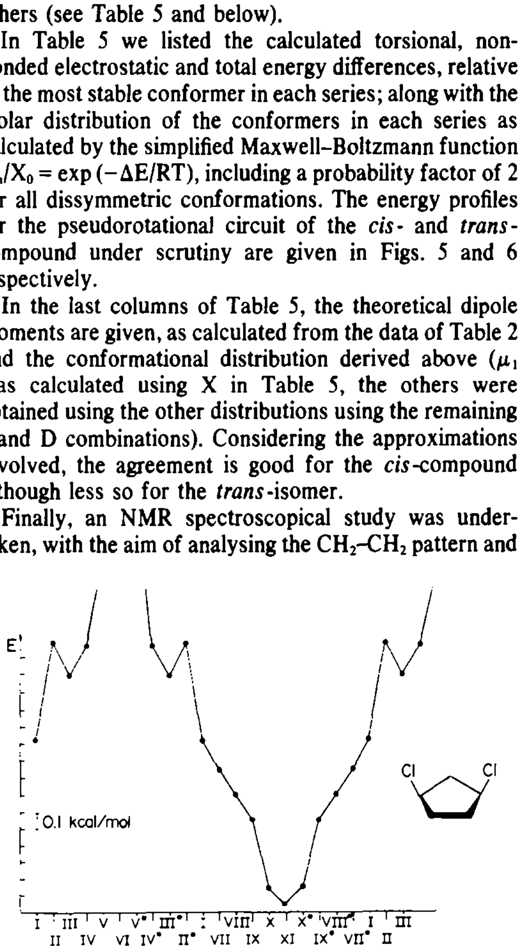

Fig. 4. The energy profile (Table 5) for the pseudorotation circuit (Fig. 1) of *cis*-1,3-dichlorocyclopentane.

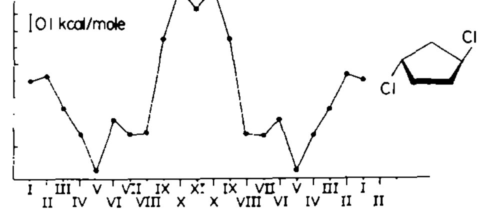

Fig. 5. The energy profile (Table 5) for the pseudorotation circuit (Fig. 2) of trans-dichlorocyclopentane.

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†There are a number of points which we feel compelled to comment on. The parameterization problem in molecular mechanics is one of the most difficult and the Achilles' heel in many a method. We faced more than one dilemma since, not being creatively active in this field, we had to make choices, albeit judicious ones, rather than offer our own solution. A certain, perhaps doubtful consolation was the finding that in various instances, investigators in this field used sometimes questionable parameters, the main argument being the obtention of reasonable results.

A number of assumptions in our work are worth mentioning. The use of basic frames on which the substituents are introduced can be defended by the fact that in many instances, the ring geometry was not or only slightly affected by introduction of small substituents.[7] This, and the fact that we refer only to energy differences between confirmations led us also to delete the bond-bending strain term from our calculation. Another point are the parameters in the non-bonded interactions term (b). In one of the most advanced force-fields available[18] it was strongly suggested to discard the old values for r*,[21,22] mainly by advocating a higher Van der Waals radius for H (1.45 Å). Lugar[7] has used a Van der Waals radius of 1.25 Å but has also raised the value of ϵ to 0.233 kcal/mole, the calibrating criterion being to make an equatorial methyl group (in methylcyclohexane) more stable than an axial one by 1.8 kcal/mole. We accept the approach as having its merits. Finally, our tribulations with the (c) term for electrostatic interactions are actually outlined in the text.

Table 4. Atomic coordinates of the possible locations of substituting chlorine atoms on cyclopentane (in Å)

	Envelope			Half-chair		
Conformation[a]	x	y	z	x	y	z
1u	−0.05	0.00	2.10	−1.01	0.23	1.47
1d	−1.63	0.00	−0.46	−1.01	−0.23	−1.47
2u	0.43	2.68	0.57	0.41	2.57	0.82
2d	0.66	1.28	−2.02	1.03	1.65	−1.92
3u	2.76	1.39	1.72	2.40	0.65	2.09
3d	3.43	1.39	−1.18	3.64	1.71	−0.42
4u	2.76	−1.39	1.72	3.64	−1.71	0.42
4d	3.43	−1.39	−1.18	2.40	−0.65	−2.09
5u	0.43	−2.68	0.57	1.03	−1.65	1.91
5d	0.66	−1.28	−2.02	0.41	−2.57	−0.81

[a] See Figs. 3 and 4; u = up; d = down.

Table 5. The relative energies and the conformational composition of *cis*- and *trans*-1,3-dichlorocyclopentane

							Calculated electric(d) dipole moments			
Conformer(a)	(a)	E_{tors}	E_{nb}	$E_{\mu\mu}$	E_{tot}	X, %(c)	μ_1	μ_2	μ_3	μ_4
E(2e–5e)	XI	0	0	0	0	18.2				
H(3e–5e')	X	46	38	−20	64	32.7				
E(1e–3bd)	IX	388	134	−34	488	16.0				
H(1bd–3e)	VIII	538	102	−9	631	12.5				
E(2e–4bu)	VII	692	75	78	845	8.7				
H(2e'–5a')	I	656	296	−7	945	7.4	2.62	2.69	2.50	2.60
H(1bu–3a)	III	538	422	795	1,755	1.8				
E(1a–3bu)	IV	388	566	1,275	2,229	0.8				
E(2a–4bd)	II	692	638	459	1,789	1.8				
H(3a–5a')	V	46	7,007	2,448	9,501	0.0				
E(2a–5a)	VI	0	12,011	2,934	14,945	0.0				
H(2a'–4e)	V	0	0	0	0	18.2				
H(2e'–4a)	VII	0	221	0	221	12.5				
E(1e–3bu)	IV	342	−87	−25	230	12.3				
E(1a–3bd)	VIII	342	−71	−40	231	12.3				
E(2a–5e)	VI	−46	345	69	368	9.8				
H(1bu–3e)	III	492	−103	−25	364	9.8	1.73	1.75	1.66	1.71
H(2e'–5e')	I	610	−52	−11	547	7.2				
E(2e–4bd)	II	646	−37	−18	591	6.7				
H(1bd–3a)	IX	492	321	−34	779	4.9				
H(2a'–5a')	XI	610	364	13	987	3.4				
E(2a–4bu)	X	646	477	4	1,119	2.7				

(a)See Figs. 1 and 2; a = "axial", e = "equatorial"; a' = "quasi-axial"; e' = "quasi-equatorial"; b = "bisectional"; d = down; u = up.

(b)Calculated using r = 1.57 Å and D = 1 (see text).

(c)Conformational equilibrium distribution (see text) in mole %.

(d)Calculated using data of Table 2 and the conformational distribution given here (μ_1) or mentioned in the text.

extract dihedral angles thereof. However, the spectra of the *cis*- and *trans*-dichlorides as well as those of the 1,3-dideutero derivatives immediately revealed the futility of these attempts. The *cis*-compound has an unresolved CH_2–CH_2 signal and the *trans*-isomer only has a narrow, albeit discernible, AA'BB' pattern.

We then turned our attention to the CHCl–CH_2–CHCl parts of the two isomers. From their NMR spectra (excluding the CHCl protons) and from the spectra of their 1,3-dideutero derivatives the chemical shifts and coupling constants were extracted (Table 6).

The question was what could be done with so little, to discern preferred conformations. The most attractive approach seems to be by way of the R value.[28,29] This method, the essentials of which are outlined in Fig. 6, has been quite successful in 6-membered rings but the pitfalls in its use for 5-membered ring compounds have been clearly put forward.[30] Thus one is led to suspect that, in those cases where the method has been indiscriminately applied to cyclopentanes or heteroanalogs, the results are either fortuitous or erroneous altogether.[31,32] The failure of the method for 5-membered rings, has been attributed[30] to the lack of 3-fold projection symmetry, since in rings with appreciable angle strain, χ becomes greater than 120°. Thus, J_{trans} is bound to increase as J_{cis} remains constant, inflating the R value and, thereby, leading to an overestimation of the internal torsional angle Ψ (Fig. 6).

One way out of this impasse is to evaluate the projection angle χ and to calculate R from the basic expression given in Fig. 6. The difficulty lies, of course, in

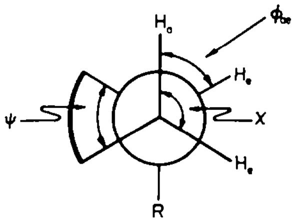

Fig. 6. Newman projection of a CH_2–CHR grouping of cyclopentane along with expressions for the torsional angles, ^3J and R of the general case and if $\chi = 120°$[30].

$$\phi_{aa} = \chi + \Psi$$

$$\phi_{ee} = \chi - \Psi$$

$$\phi_{ae} = \phi_{ea} = \Psi$$

$$^3J_{HH} \cong A\cos^2\phi \text{ (Karplus)}$$

$$R = \frac{J_{trans}}{J_{cis}} = \frac{\frac{1}{2}[\cos^2(\chi + \Psi) + \cos^2(\chi - \Psi)]}{\cos^2\Psi}$$

$$\Psi = \arccos\left[\frac{1 - \cos 2\chi}{2(R - \cos 2\chi)}\right]^{1/2}$$

$$\text{for } \chi = 120°\text{: } R = \frac{3 - 2\cos^2\Psi}{4\cos^2\Psi} \quad \text{and} \quad \Psi = \arccos\left[\frac{3}{2+4R}\right]^{1/2}$$

Table 6. The NMR spectral parameters of *cis*- and *trans*-dichlorocyclopentane (the CHCl–CH_2–CHCl grouping)[a]

cis-	$\delta_A = 2.75$; $\delta_B = 2.22$; $\delta_X = 4.19$; $J_{AB} = -15$; $J_{AX} = 7.5$; $J_{BX} = 5.5$
trans-	$\delta_A = 2.46$; $\delta_X = 4.48$; $J_{AX} = J_{AX'} = 5.4$

[a] In CCl_4 (*ca.* 10%). Chemical shifts (δ) are in ppm relative to TMS. Coupling constants (J) are in Hz.

finding an accurate and reliable method to do this for a system like ours, where a multitude of conformations has to be analysed for the appropriate projection angles χ.

Another alternative is offered by the simplified Karplus equation[33] (where the small, last two terms have been neglected) (Fig. 6), only that this method is plagued by the problem of dependence of A on ring strain and substituent electronegativities. An attempt to use this latter approach on 5-membered rings has been made,[30] taking the average torsional angle of cyclopentane as 27° (from molecular mechanics and electron diffraction data) and calculating an A value of 9.95. This was subsequently used for the saturated CH_2–CH_2 grouping in a number of 5-membered rings.[30]

We have undertaken to apply both methods, after making some inevitable approximations. The bond angles were calculated for all conformers in the pseudorotational circuits of *cis*- and *trans*-dichlorocyclopentane, using vector analytical techniques on the geometries described above and hence, the same degree of accuracy obtains. A sample result is given in Fig. 7 for conformer IV of *cis*-dichlorocyclopentane. The respective coupling constants were then calculated (Fig. 7), using a constant A of 10.0. The rationale for using this A was provided by Lambert's argument[30] (*vide supra*) on the one hand and substituent electronegativity considerations on the other. The latter have been discussed[34–37] in terms of correlation of J with the electronegativity of substituents and their orientation in space relative to the vicinal protons. In a most recent study,[34] a relationship was put forward between the *gauche* coupling constant J_g and the (Huggins[38]) electronegativity difference ΔX between the substituent and hydrogen, with impressive agreement with experiment. We have applied the method to some of our conformers and came up with an average A value of 10.1, which explains our choice above.

In Table 7 we present the resulting coupling constants

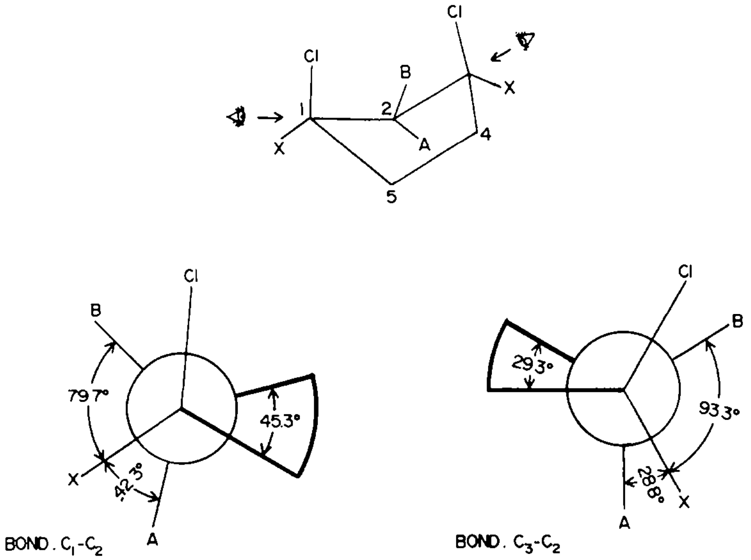

Fig. 7. A sample evaluation of J_{AX} and J_{BX} for conformer IV (Fig. 1) of *cis*-1,3-dichlorocyclopentane using calculated dihedral angles (see text).

$$J_{AX}/A = \frac{1}{2}\cos^2(42.3°) + \frac{1}{2}\cos^2(28.8°) = 0.66$$

$$J_{BX}/A = \frac{1}{2}\cos^2(79.7°) + \frac{1.11}{2}\cos^2(93.3°) = 0.018$$

Table 7. Calculated vicinal coupling constants in the grouping CHCl–CH_2–CHCl of 1,3-dichlorocyclopentanes(a)

Isomer	*cis*			*trans*		
Conformer(b)	J_{cis}	J_{trans}	R(c)	J_{cis}	J_{trans}	R(c)
I	9.3	3.6	0.38	9.4	6.3	0.67
II	8.8	1.7	0.19	8.8	6.0	0.68
III	7.7	0.55	0.07	7.3	5.6	0.77
IV	6.5	0.2	0.03	6.1	5.4	0.88
V	4.8	0.3	0.07	4.8	5.6	1.17
VI	4.4	0.3	0.08	4.9	5.6	1.14
VII	8.8	6.0	0.68	5.2	5.4	1.04
VIII	7.1	8.3	1.17	6.2	4.5	0.69
IX	6.0	9.6	1.60	7.6	3.2	0.42
X	5.2	10.7	2.05	8.8	1.7	0.19
XI	5.5	10.8	1.96	9.2	1.0	0.11
Av.(d)	6.7	4.7	0.70	7.1	5.0	0.71
BD(e)	6.4	8.9	1.39	6.5	5.5	0.85
Obs.	5.5	7.5	1.36	5.4	5.4	1.00

(a)Calculated using the Karplus equation (Fig. 6) with A = 10.0 (see text).

(b)The Roman numbers stand for the various conformers in the respective pseudorotational circuits (Figs. 1 and 2).

(c)$R = J_{trans}/J_{cis}$.

(d)Calculated by $\Sigma J/11$, i.e. assuming no conformational preference.

(e)Calculated by summation of the various J's multiplied by the respective Boltzmann distribution factors (Table 5).

for all the conformers in both the *cis*- and *trans*-isomer, along with the corresponding R values. At once we see that, in the *cis* case, the observed $^4J_{cis}$ and $^4J_{trans}$ do not fit any single conformer nor the simple average of calculated values. However, the averaged coupling constants over the Boltzmann distribution of *cis* conformers given in Table 5, though a bit high, lead to an R value which agrees well with the experimental R. These relatively large J_{BD} values (both in the *cis* and *trans* cases) are probably due to a somewhat overestimated A constant, which however cancels out in the R value and hence, the latter's agreement with experiment. The situation in the *trans* isomer is less satisfactory. The observed R value is 1.0 in the rapidly inverting *trans*-CHCl–CH_2–CHCl grouping in the framework of the pseudorotational circuit (Fig. 2). We must rely therefore on the averaged J_{BD} themselves and there the agreement is modest. On the whole, however, one can conclude that these results indicate again that we deal with a multitude of equilibrating conformations rather than with single, defined ones.

DISCUSSION

The problem of conformational structure and homogeneity of cyclopentane derivatives has preoccupied many investigators. We shall confine ourselves to a discussion of halogen derivatives. Early calculations of *mono*-halogenocyclopentanes[4,39,16] have led to the conclusion that the barriers to pseudorotation should be small (~ 1 kcal/mole) and that a multitude of conformations seem to be populated. IR[39,40a] and Raman[40a] spectroscopical data lend support to this assertion by their broad and diffuse character. Furthermore, it was contended[16,40a] that the halogen apparently occupies the most puckered part of the ring and that it is, moreover, in axial conformation. Subsequently, however, more refined (temperature-[41a,42c,43] and phase-dependent) IR and Raman studies of (*inter alia*) chlorocyclopentane confirmed a low barrier to pseudorotation[41b] and indicated that conformations with both axial and equatorial chlorines occur at room temperature, and low enthalpy differences ("neat"—344 cal/mole;[41b] CS_2 solution—700 cal/mole[42c]) were evaluated, albeit in favor of the axial conformation. We feel that this situation has been overinterpreted, as expressed in statements, e.g. "most investigators agree that the chloro-, bromo- and iodocyclopentane molecules are bent with the halide in the axial position of the flap".[41d] For one, the terms "axial" and "equatorial" in the context of such conformational analytical studies of cyclopentane derivatives have qualitative meaning, at best. Thus, the broad 590 cm^{-1} Raman line in chlorocyclopentane has been assigned to the "axial" C–Cl stretching absorption,[40a] on the basis of an empirical set of parameters following which, a truly axial C–Cl bond is supposed to absorb up to 685 cm^{-1}.[40b] Similarly, the second absorption at 614 cm^{-1} which appears as a resolved band at low temperatures[41a,42a,c] was interpreted as that of an "equatorial" chlorocyclopentane whereas a truly equatorial C–Cl bond is supposed to stretch at about 742 cm^{-1}.[40b] We think, therefore, that no definite conformational assignments are possible on the strength of the vibrational spectroscopical data, other than saying that chlorocyclopentane (as well as other monohalogen derivatives) exist in a multitude of conformations with certain preferred ones in one (or more) potential well of the pseudorotational circuit in which low barriers prevail. NMR studies[31d,40a,41d] could, in fact, add nothing more conclusive to this statement.

Another series which has received attention is that of *trans*-1,2-dihalogeno-5-membered rings,[14–16] for which diaxial conformations have been largely concluded. We shall, however, not dwell on this subject, mainly because vicinal steric and polar effects may obscure, in our opinion, the role of ring conformational modes. We note, though, that even there small energy minima and relatively high degrees of pseudorotation (or pseudolibration) occur.[16a]

We interpret now our own results by drawing, what we think as an obvious conclusion, that no conformational exclusivity for one form can be claimed for *cis*-1,3-dichlorocyclopentane but rather a portion of the pseudorotational circuit is preferentially populated. In this well we find the forms X and XI (Fig. 1) and a few tenths of a kcal. higher VIII and IX. In the *trans* isomer the wells are even less deep and steep and conformation V (Fig. 2) along with I–VIII are probable. In fact, we want to point out that these forms are not necessarily existing in reality and that probably intermediate forms actually occur. The temperature dependent behavior of both isomers as scrutinized by NMR spectroscopy indicate also low barriers to pseudorotation.

This is actually in accord with previous qualitative results in this series[1,2] in which 1,3-substituted cyclopentanes have been found to be of equal energy and to exhibit strikingly similar physical properties as well as chemical behavior.

We strongly recommend therefore, to avoid such terms as "envelopes" and "half-chairs", "axial" and "equatorial" when discussing real conformations of simply substituted, mobile 5-membered rings.

EXPERIMENTAL

The NMR spectra were measured (in $CDCl_3$ or CCl_4) on a Varian HA-100 or a Jeol C-60 HL instrument. GLC was performed on a

Varian 1800 gas chromatograph using analytical or preparative columns.

Computations were carried out on the CDC-6000 computer of the Tel-Aviv University Computation Center.

cis- *and* trans-1,3-*Dichlorocyclopentane*

The disilver salt of *cis*- or *trans*-cyclopentane-1,3-dicarboxylic acid was prepared[44] from 5 g acid, 61 ml 1 NH NaOH and 11 g silver nitrate. The product was dried over night *in vacuo* over P_2O_5 at 75°. The dry salt (11 g) was suspended in 20 ml dry nitrobenzene and a soln of 4.6 g chlorine in 40 ml dry nitrobenzene was added dropwise with mechanical stirring at 0°. After 1 hr stirring at 0° and another hr at room temp, the mixture was filtered and the solid washed with warm CCl_4. The filtrate was fractionated at 30 torr. The fractions boiling up to 80° were collected and redistilled, b.p. *cis*—100°/70 torr, *trans*—86°/70 torr, identical with the respective products obtained by the method of Russel and Ito.[6] The pure isomers were obtained by preparative GLPC (DEGA column, 110°).

The 1,3-dideutero derivatives were prepared analogously, starting with the corresponding 1,3-dideutero-1,3-cyclopentane dicarboxylic acids.

Dipole moments

The Hedestrand method[45] was used. This is applicable when for dilute solutions of the substance in non-polar solvents (0–5 mole %), their densities (ρ), the square of their refractive indexes (n^2) and their dielectric constants (ϵ) depend linearly on the molar fraction of solute. Under these conditions, that were found to be fulfilled in the cases investigated, the molar polarization and the molar refraction, $P_M{}^0$ and $R_M{}^0$, of the substance (values extrapolated to infinite dilution) can be expressed in terms of the slopes and of the intercepts of the experimentally determined (and calculated by the least-squares method) straight lines. The calculation of the dipole moment μ in Debye units at the absolute temperature T follows immediately: $\mu = 0.0128[(P_M{}^0 - R_M{}^0)T]^{1/2}$.

The densities of the solns were determined by picnometry, the refractive indexes by means of a Bausch and Lob Abbé type refractometer and the dielectric constants by means of a high-frequency (0.1–12 MHz range) Multi Dekameter Model DK 06 capacity bridge. The results are given in Table 8.

Table 8. Results from dipole moment measurements (25°C)

Cyclopentane	Solvent	$P_M{}^0$	$R_M{}^0$	μ, D
cis-1,3-dichloro	CCl_4	183.76	33.12	2.73
cis-1,3-dichloro	C_6H_6	187.57	32.93	2.76
trans-1,3-dichloro	CCl_4	74.75	38.81	1.44
trans-1,3-dichloro	C_6H_6	73.65	31.68	1.44
cis-1,3-dicyano	CCl_4	445.04	33.18	4.51
cis-1,3-dicyano	C_6H_6	478.13	31.20	4.70
cis-1,3-dicyano	1,4-dioxane	480.65	32.13	4.70
trans-1,3-dicyano	CCl_4	190.08	31.80	2.78
trans-1,3-dicyano	C_6H_6	198.62	31.39	2.86
trans-1,3-dicyano	1,4-dioxane	198.95	29.86	2.87

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