

1023. The Conformation of 4-Substituted Epoxycyclopentanes

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Dipole moments of some 4-substituted epoxycyclopentanes indicate that the carbon ring is buckled. The two-ring system in most of the compounds is boat-shaped, but one proves to be chair-shaped. Explanations of these observations are suggested.

CYCLOPENTANE is probably non-planar.¹⁻³ Cyclopent-1-ene is found from its microwave spectrum⁴ to have ring atom 4 (cf. diagram I) out of the plane of the other four atoms. Epoxycyclopentane⁵ and epoxycyclohexane⁶ have similarly been shown to have the four carbon atoms in, and adjacent to, the epoxy-ring coplanar, but the other two atoms of the carbon ring in the latter compound are out of this plane, one being above it and the other below, while in the former the conformation is not entirely certain although the results are consistent with ring atom 4 being in this plane. The electric dipole moments of some 4-substituted derivatives of epoxycyclopentane are now reported and used to obtain the conformations of the carbon rings.

Measurements of dielectric constant (ϵ), specific volume (v) and refractive index (n) have been made on dilute solutions of weight fraction (w) in dry benzene at 25°. Results have been calculated by the method of Halverstadt and Kumler⁷ using (R. J. B.) both the measured molar refraction, $[R_D]$ (obs.), and the molar refraction calculated from tables of bond refractions,⁸ $[R_D]$ (calc.), as the molar distortion polarisation, the mean value of the moment being used in the Discussion; or (G. M. G.) the measured molar refraction as the molar distortion polarisation.

DISCUSSION

From the moments of the disubstituted cyclopentanes and those of the appropriate monosubstituted ones, the angles between the dipole axes can be calculated (see θ , in Table 2). By using structural information from the microwave investigation of epoxy-cyclopentane,⁵ *viz.*, that the angle between the plane of the epoxy-ring and that of ring atoms 1,2,3,5 is 98°, and by assuming that the bond to the polar 4-substituent makes an angle of 54.75° with the plane of atoms 3,4,5, the dihedral angle, ϕ (in Table 2), between this plane and that of atoms 1,2,3,5 [see diagrams (IIa and b)] is then calculated. ϕ is defined as positive when ring atom 4 is on the same side of plane 1,2,3,5 as the oxygen atom, *i.e.*, when the two-ring system is boat-shaped, and negative when it is chair-shaped. The

¹ A. Allmeningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, 1961, **15**, 711.

² I. F. Laurenson and F. A. Rushworth, *Proc. Phys. Soc.*, 1958, **72**, 791.

³ K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, 1959, **81**, 3213.

⁴ G. W. Rathjens, *J. Chem. Phys.*, 1962, **36**, 2401.

⁵ G. Erlandsson, *Arkiv Fysik*, 1955, **9**, 341.

⁶ B. Ottar, *Acta Chem. Scand.*, 1947, **1**, 283.

⁷ I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

⁸ A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J.*, 1952, 514.

TABLE I
Physical properties of cycloalkane derivatives

(R. J. B.)	10^6w	ϵ	v	n	10^6w	ϵ	v	n
	0	2.2741 ⁹	1.1446 ¹⁰	1.4980 ¹⁰				
<i>4β-Cyano-4α-methylepoxycyclopentane</i>								
<i>Epoxycyclopentane</i>					445	2.2854	1.1445	1.49801
632	2.2767		1.1445	1.49796	1130	2.3030	1.1443	—
1556	2.2810		1.1446	1.49781	1558	2.3131	1.1443	1.49800
2871	2.2878		1.1444	1.49777	2305	2.3376	1.1439	1.49790
5253	2.3002		1.1444	1.49755				
<i>4-Cyanotetrahydropyran</i>								
<i>Cyanocyclopentane</i>					910	2.2818	1.1445	1.49791
3969	2.3349		1.1443	1.49793	2108	2.2900	1.1444	—
5025	2.3524		1.1443	1.49781	4283	2.3098	—	1.49784
9463	2.4211		1.1440	—	8910	2.3487	1.1431	1.49457
11,784	2.4562		1.1439	1.49755	(G. M. G.) 0	2.2750	1.1447	1.4980
<i>4α-Bromoepoxycyclopentane</i>								
1851	2.2784		1.1438	1.49803	<i>4α-Cyanoepoxycyclopentane</i>			
3253	2.2818		—	1.49800	1017	2.2833	1.1446	1.49799
4697	2.2852		1.1424	1.49800	1904	2.2904	1.1444	1.49798
<i>4β-Bromoepoxycyclopentane</i>								
279	2.2764		1.1445	1.49804	3576	2.3044	1.1440	1.49794
523	2.2786		1.1443	1.49804	5023	2.3160	1.1435	1.49793
1971	2.2908		1.1435	1.49804	<i>4β-Cyanoepoxycyclopentane</i>			
<i>4α-Cyano-4β-methylepoxycyclopentane</i>								
559	2.2774		1.1445	1.49797	1096	2.3056	1.1444	1.49800
2028	2.2869		1.1443	1.49793	1980	2.3304	1.1441	1.49799
3780	2.2977		1.1438	1.49784	3557	2.3745	1.1436	1.49798
7346	2.3206		1.1432	1.49778	4357	2.3965	1.1433	1.49797
$d\epsilon/dw$	dv/dw	dn/dw	$\tau P_{2\infty}$	$[R_D]$ (obs.)/ $[R_D]$ (calc.)	μ (D)			
<i>Epoxycyclopentane</i>								
4.9	-0.05	-0.08	104.9	24.0	1.99 ± 0.02			
±0.1	±0.01	±0.01		23.0	2.00 ± 0.02			
<i>Cyanocyclopentane</i>								
15.50	-0.060	-0.038	308.0	28.2	3.70 ± 0.01			
±0.05	±0.002	±0.001		27.7	3.70 ± 0.01			
<i>4α-Bromoepoxycyclopentane</i>								
2.37	-0.46	0.00	105.9	32.7	1.89 ± 0.02			
±0.01	±0.02			30.7	1.92 ± 0.02			
<i>4β-Bromoepoxycyclopentane</i>								
8.5	-0.56	0.00	288.9	27.9	3.57 ± 0.03			
±0.1	±0.02			30.7	3.55 ± 0.03			
<i>4α-Cyano-4β-methylepoxycyclopentane</i>								
6.30	-0.20	-0.035	180.5	31.6	2.70 ± 0.01			
±0.05	±0.01	±0.005		32.1	2.70 ± 0.01			
<i>4β-Cyano-4α-methylepoxycyclopentane</i>								
26	0.25	0.00	634.7	32.3	5.4 ± 0.1			
±1	±0.05			32.1	5.4 ± 0.1			
<i>4-Cyanotetrahydropyran</i>								
8.36	-0.17	-0.05	214.4	29.6	3.02 ± 0.02			
±0.03	±0.05	±0.02		29.5	3.02 ± 0.02			
<i>4α-Cyanoepoxycyclopentane</i>								
8.183	-0.24	-0.015	199	28.3	2.89 ± 0.01			
<i>4β-Cyanoepoxycyclopentane</i>								
27.92	-0.32	0.007	605	27.0	5.33 ± 0.01			

⁹ L. Hartshorn, J. V. L. Parry, and L. Essen, *Proc. Phys. Soc.*, 1955, **68B**, 422.

¹⁰ J. Timmermans, "Physico Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

calculations should be made with allowance for induced moments, and this has been done¹¹ using group refractions, *viz.*, oxygen 3.08, cyano-group 4.82, bromo-group 9.39 c.c. (values calculated neglecting induced moments are given in parentheses). The compounds with the polar substituent on ring atom 4 *trans* to the epoxy-group are termed α -compounds, those with it *cis* are β -compounds

The results show that the α - and the β -4-cyano-derivatives, with either H or CH₃ in the 4 β - and the 4 α -positions, respectively, as well as the 4 α -bromo-derivative, all have boat

TABLE 2
Dipole moments and derived stereochemistry of epoxycyclopentanes

Compound	μ (D)	(Ref.)	Angle between dipoles θ	Dihedral angle ϕ	Group
Epoxycyclopentane ...	2.00 \pm 0.2	(a)			
Cyanocyclopentane ...	3.70 \pm 0.01	(a)			
Bromocyclopentane ...	2.21 \pm 0.02	(b)			
4 α -Cyano Q	2.89 \pm 0.01	(a)	129.75° (129°)	23° (24°)	A
4 β -Cyano Q	5.33 \pm 0.01	(a)	39.75° (43.5°)	3.5° (0°)	A
4 α -Bromo Q	1.91 \pm 0.01	(a)	124.5° (126°)	28.25° (26.5°)	A
4 β -Bromo Q	3.56 \pm 0.01	(a)	57.5° (64.5°)	-14.25° (-21°)	B
4 α -Cyano-4 β -methyl Q	2.70 \pm 0.01	(a)	135° (135°)	17.75° (18°)	A
4 β -Cyano-4 α -methyl Q	5.4 \pm 0.1	(a)	33.5° (39°)	9.75° (4°)	A

Q = Epoxycyclopentane. (a) Present work. (b) Data from ref. 12 recalculated.

conformations: these form group A. Only the 4 β -bromo-derivative has a chair conformation (group B). The energies which could determine conformations are those due to (i) rotation about ring bonds, (ii) changes of bond angles, (iii) steric repulsion between fourth or higher neighbours, and (iv) dipole-dipole interactions. These are considered below.

(i) Diagrams (III) and (IV) show views along ring bonds joining atoms 4-3 and 3-2, respectively, in the *plane* ring conformation of epoxycyclopentane (I). There are corresponding views along the 4-5 and 5-1 axes. Diagram (III) shows that there are six pairs of fully eclipsed bonds in this conformation. From the rough value ascribed to the barrier to rotation about the central C-C bond in n-butane (*ca.* 2.8 kcal. mole⁻¹),¹³ cf. the rotation barriers in ethane 2.9^{13,14} and in propane 3.4,¹³ it may be inferred that the loss of energy per pair of eclipsed bonds on going to a staggered conformation is about 1 kcal. mole⁻¹. If the ring buckles to make a two-ring boat or chair form, eclipsing is reduced and some of this stability is gained. In the 4-cyano-4-methyl compounds, however, either distortion would do this equally well and so neither is favoured. In the *cis*(β)-compounds distortion to a chair-type, and in the *trans*(α)-compounds distortion to a boat-type is probably slightly favoured because this gives a *trans* instead of a *gauche* conformation to the bonds shown in diagram (III).

(ii) Buckling would decrease the average ring bond angle from 108° and so would increase bond angle strain energy which is a minimum in the planar conformation, but buckling to give $\phi = \pm 10^\circ$ only causes a decrease of 0.25° per bond angle which for a bending force constant¹⁵ of 17.5 cal. mole⁻¹ degree⁻² means an increase of energy of only 0.005 kcal. mole⁻¹. Comparatively small interactions can therefore cause buckling. In diagram (IV) the direction of the bond from ring atom 2 to H' is assumed to be the same as that of the corresponding bond in ethylene oxide. This bond is, therefore, partly eclipsed in the plane conformation by the bond from atom 3 to H''. Buckling to a boat form (clockwise rotation of atoms 4, H, H'') would reduce this particular energy in two

¹¹ J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955.

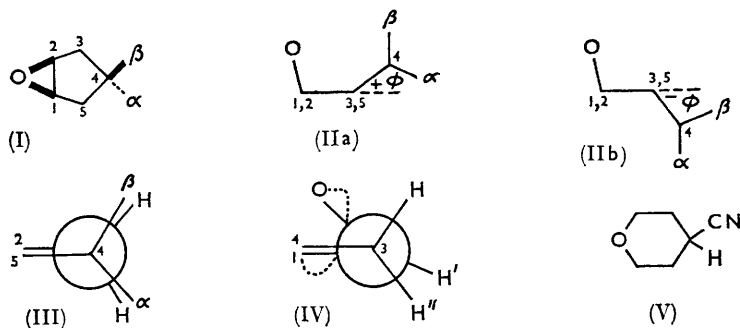
¹² M. T. Rogers and J. D. Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 843.

¹³ K. S. Pitzer, *Discuss. Faraday Soc.*, 1951, **10**, 66.

¹⁴ D. R. Lide, *J. Chem. Phys.*, 1958, **29**, 1426.

¹⁵ F. H. Westheimer, "Steric Effects in Organic Chemistry," ed. M. S. Newman, Wiley, New York, 1956.

bonds per molecule, but buckling to a chair form (anti-clockwise rotation) would increase it. The diagram also shows complete eclipsing of bonds 3-4 and 2-1, but if the latter is really a bent¹⁶ or "banana" bond with the electron charge cloud centred round the broken line



instead of the full one, and if also the 2-O bond is to be similarly represented, then interaction of bond 3-4 with 2-1 and 2-O would be reduced by clockwise rotation but increased by the opposite. These two sets of interactions both favour a boat conformation.

(iii) Comparison of calculated distances between fourth neighbouring groups across the ring (*e.g.*, β -Br or centre of β -CN, and O) with sums of van der Waals radii indicate that the steric repulsion forces, even for β -Br, are not likely to be large enough to decide conformation.

(iv) Calculations which treat the dipoles as charge doublets with formal charges placed on atoms (epoxy-dipole 1 Å long with negative end at O, cyano-dipole 1.16 Å long with negative end at N, bromo-dipole 1.94 Å long with negative end at Br) show that for the compounds in group A the change in dipole-dipole energy with change in conformation is small, *e.g.*, <0.05 kcal. mole⁻¹ for a change from the planar conformation to a boat with $\phi = +10^\circ$. In the *trans*(α)-compounds the separation of the polar groups is 4-5 Å so this insensitivity is to be expected. In the 4- β -cyano-compounds the negative end of the epoxy-dipole is only ~ 3 Å from positive end of the cyano-dipole, so the dipole-dipole energy very slightly favours the boat conformation (-0.05 kcal. mole⁻¹, with $\phi = +10^\circ$). Although dipole-dipole attraction may provide additional stabilisation of the boat conformation in this case, it does not cause the related monocyclic compound, 4-cyanotetrahydropyran (V; obs. $\mu = 3.02$ D see Table 1) to adopt a similar conformation. The chair-shaped conformation has calculated $\mu = 3.08$ D (with either an axial or an equatorial nitrile group) and so is the actual one. The analogy is, however, not perfect. In the 4 β -bromo compound the dipole-dipole energy is increased by 0.2 kcal.mole⁻¹ when a boat conformation with $\phi = +10^\circ$ is formed from a planar one, *i.e.*, there is repulsion.

Consideration of these energies suggests that there is a marked tendency for the carbon ring to buckle and that the boat form is generally favoured by the torsional energies about bonds 3-2 and 5-1, but if the dipole-dipole energy or the steric energy is large enough, as it may be for a β -substituted compound, the chair conformation is the more stable. On this basis, epoxy-cyclopentane is predicted to have a boat conformation.

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¹⁶ C. A. Coulson, "Valence," 2nd edn., 1961, Oxford, p. 216.