

SHORT COMMUNICATIONS

MOLECULAR POLARIZABILITY ANISOTROPY OF CYCLOPROPANE*

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Specification of the optical polarizability ellipsoid of the cyclopropane system is an essential prerequisite for the investigation by the Kerr effect technique of conformational isomerism in molecules containing the cyclopropyl grouping. The principal electron polarizabilities of the cyclopropane ellipsoid can be obtained directly from the molar Kerr constant and the electron polarization (using equations 22, 27, and 30 of ref.¹) since, from symmetry, $b_1 = b_2 \neq b_3$, where b_1 and b_2 are the in-plane polarizabilities and b_3 is directed perpendicularly to the plane of the three carbon atoms. The appropriate solution-state measurements from which the molar Kerr constant ${}_mK(\text{C}_3\text{H}_6)$ can be derived are summarized in Tables 1 and 2.

Experimental

Cyclopropane gas (>99% purity) from the Matheson Co., U.S.A., was dried over KOH pellets before being passed into weighed amounts of solvent.

Apparatus, techniques, symbols used, and methods of calculation have been described before.²⁻⁴ The quantities $\Delta\epsilon$, Δd , Δn , and ΔB are the differences found between the dielectric constants, densities, refractive indices, and Kerr constants respectively, of the solutions containing weight fractions w_2 of solute and of the appropriate solvent. The following data apply at 25° for the solvents used:

	ϵ_1	d_1	$(n_1)_D$	$10^7 B_1$	$10^{12} K_1$
Cyclohexane	2.0199	0.77389	1.4235	0.059	0.0147
Benzene	2.2725	0.87378	1.4973	0.410	0.0756

Discussion

Ramaswamy⁵ has recorded the electron polarization of cyclopropane as 13.93 c.c. from which the sum $b_1 + b_2 + b_3$ is calculable as 16.56. § Substitution of the quantities ${}_mK = 1.0 \times 10^{-12}$, ${}_D P = {}_\infty P_2 = 14.5$, and ${}_E P = 13.93$ in equations 27 and 30 of ref.¹ leads to a polarizability anisotropy ($b_1 - b_3$) of ± 1.45 . Thus two possible sets of molecular polarizability semi-axes emerge for cyclopropane:

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§ The polarizability semi-axes of bonds or groups b_L , b_T , or b_V or of molecules b_1 , b_2 , or b_3 are quoted throughout in Å³ units.

¹ Le Fèvre, R. J. W., *Adv. phys. org. Chem.*, 1965, 3, 1.

² Le Fèvre, C. G., and Le Fèvre, R. J. W., Ch. XXXVI in "Physical Methods of Organic Chemistry." (Ed. A. Weissberger.) 3rd Edn. (Interscience: New York 1960.)

³ Le Fèvre, R. J. W., "Dipole Moments." 3rd Edn. (Methuen: London 1953.)

⁴ Le Fèvre, R. J. W., and Sundaram, K. M. S., *J. chem. Soc.*, 1962, 1494.

⁵ Ramaswamy, K. L., *Proc. Indian Acad. Sci. A*, 1936, 4, 675.

$b_1 = b_2 = 6.00$ and $b_3 = 4.55$ or alternatively $b_1 = b_2 = 5.04$ and $b_3 = 6.49$. The error in the experimental molar Kerr constant results in an uncertainty of ± 0.02 in b_1 and b_2 and ± 0.05 in b_3 for each set of axes. The magnitude of our optical polarizability anisotropy for cyclopropane as a solute is larger than the value of ± 0.807 , obtained by Bridge and Buckingham⁶ from measurements of the depolarization ratio of Rayleigh scattering from cyclopropane gas (using light of wavelength

TABLE 1

INCREMENTAL DIELECTRIC CONSTANTS, DENSITIES, REFRACTIVE INDICES, AND KERR CONSTANTS FOR SOLUTIONS AT 25°

<i>Cyclopropane in Cyclohexane</i>						
$10^5 w_2$	3012	3487	3515	3710	4453	
$-10^4 \Delta \epsilon$	81	93	103	98	134	
$-10^5 \Delta d$	601	704	680	749	882	
$-10^4 \Delta n$	30	38	38	40	49	
	whence $\Sigma \Delta \epsilon / \Sigma w_2 = -0.28$, $\Sigma \Delta d / \Sigma w_2 = -0.199$, $\Sigma \Delta n / \Sigma w_2 = -0.107$					
$10^5 w_2$	3559	3595	3840	4357		
$10^{10} \Delta B$	1	0	0	0		
	whence $\Sigma 10^7 \Delta B / \Sigma w_2 = 0.007$					
<i>Cyclopropane in Benzene</i>						
$10^5 w_2$	1809	2524	2852	3083	3320	3408
$-10^4 \Delta \epsilon$	117	166	178	—	207	210
$-10^5 \Delta d$	540	756	864	—	1021	1028
$-10^4 \Delta n$	33	47	53	—	64	64
$-10^{11} \Delta B$	80	100	101	119	116	112
	whence $\Sigma \Delta \epsilon / \Sigma w_2 = -0.63$, $\Sigma \Delta d / \Sigma w_2 = -0.302$, $\Sigma \Delta n / \Sigma w_2 = -0.187$, $\Sigma 10^7 \Delta B / \Sigma w_2 = -0.37$					

TABLE 2

POLARIZATIONS, REFRACTIONS, DIPOLE MOMENTS, AND MOLAR KERR CONSTANTS OF CYCLOPROPANE IN CYCLOHEXANE AND BENZENE

Solvent	α_{E1}	β	γ	δ	${}_{\infty}P_2$ (c.c.)	R_D (c.c.)	μ (D)	$10^{12} \omega (mK_2)$
C_3H_6	-0.28	-0.257	-0.075	0.1	14.5	14.3	0	1.0 ± 0.1
C_6H_6	-0.63	-0.346	-0.125	-0.90	14.3	14.5	0	2.8 ± 0.3

6328 Å). The C_3H_6 gas anisotropy together with ${}_E P(C_3H_6) = 13.93$ c.c.⁵ leads to $b_1 = b_2 = 5.79$ and $b_3 = 4.98$ or $b_1 = b_2 = 5.25$ and $b_3 = 6.06$. The differences between the polarizabilities from the Kerr effect and those derived from the scattered light data may be attributed to a state-dependence of the molecular anisotropy and/or to our neglect of possible hyperpolarizability contributions⁷ to the Kerr effect. Buckingham, Prichard, and Whiffen⁸ have recently measured the molar Cotton-

⁶ Bridge, N. J., and Buckingham, A. D., *Proc. R. Soc. A*, 1966, **295**, 334.

⁷ Buckingham, A. D., and Orr, B. J., *Q. Rev. chem. Soc.*, 1967, **21**, 195.

⁸ Buckingham, A. D., Prichard, W. H., and Whiffen, D. H., *Trans. Faraday Soc.*, 1967, **63**, 1057.

Mouton constant of gaseous cyclopropane from which they evaluate the anisotropy of magnetic susceptibility $k_3 - k_1$ as -32×10^{-30} e.m.u., i.e.

$$\Delta K = K_3 - K_1 = -19.3 \times 10^{-6} \text{ c.c./mole,}$$

on the basis that $b_3 - b_1$ is negative. Their assignment of the sign of the magnetic anisotropy is qualitatively consistent with evidence from p.m.r. studies⁹⁻¹² of cyclopropane derivatives which have clearly established the existence of a region of high shielding above the plane of the three carbon atoms. If $b_1 > b_3$, the negative sign of ΔK is also consistent with the predictions of an approximate quantum mechanical relationship (see equation 41 of ref.¹³) connecting anisotropies of diamagnetic susceptibility and electric polarizability. Thus we conclude that for cyclopropane (as a solute in cyclohexane) $b_1 = b_2 = 6.0$ and $b_3 = 4.5_5$.

The electron polarizabilities of the three-carbon nucleus $b_i(n)$ may be extracted from the molecular b values by deducting six C-H contributions [using $b_L(\text{C-H}) = b_T(\text{C-H}) = b_V(\text{C-H}) = 0.65$]¹⁴ to give $b_L(n) = b_T(n) = 2.1$ and $b_V(n) = 0.6_5$. If each C-C bond is assumed to be axially symmetric about the intercentre line then the C-C bond parameters follow as $b_L = 1.1_3$, and $b_T = b_V = 0.2_2$ [cf. the semi-axes found¹⁴ for $\text{C}(sp^3)\text{-C}(sp^3)$ for which $b_L = 0.97$, and $b_T = b_V = 0.26$]. Alternatively if the saturated C-C aliphatic bond ellipsoids are regarded as applicable to the cyclopropane system then by additivity the polarizability parameters of the carbon nucleus are calculated as $b_L(n) = b_T(n) = 1.8_5$, and $b_V(n) = 0.7_8$. The differences $\Delta b_i = b_i(\text{obs.}) - b_i(\text{calc})$ are $\Delta b_L(n) = \Delta b_T(n) = +0.2_5$ and $\Delta b_V(n) = -0.1_3$, i.e. the polarizability and hence the electron mobility in the plane of the carbon nuclei is greater than that predicted for a system composed of saturated carbon-carbon sigma bonds alone.

Finally we note that $\infty(mK_2)$ and hence the apparent molecular anisotropy of cyclopropane is greater in benzene than in cyclohexane. We attribute this¹⁵ to the formation of a very weak cyclopropane : benzene collision complex, stabilized by normal van der Waals interactions, in which there is a tendency for the C_3 axis of the cyclopropane to be coincident with the C_6 axes of neighbouring benzene molecules. The degree of such association would be small since the upfield shift of the cyclopropane protons in benzene relative to cyclohexane is less than 0.1 p.p.m. (using tetramethylsilane as internal reference).

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⁹ Patel, D. J., Howden, M. E. H., and Roberts, J. D., *J. Am. chem. Soc.*, 1963, **85**, 3218.

¹⁰ Burke, J. J., and Lauterbur, P. C., *J. Am. chem. Soc.*, 1964, **86**, 1870.

¹¹ Forsen, S., and Norin, T., *Tetrahedron Lett.*, 1964, 2845.

¹² Pierre, J., and Arnaud, P., *Bull. Soc. chim. Fr.*, 1966, 1690.

¹³ Buckingham, A. D., *Q. Rev. chem. Soc.*, 1959, **13**, 183.

¹⁴ Le Fèvre, R. J. W., Orr, B. J., and Ritchie, G. L. D., *J. chem. Soc. (B)*, 1966, 273.

¹⁵ Le Fèvre, R. J. W., Radford, D. V., Ritchie, G. L. D., and Stiles, P. J., *J. chem. Soc. (B)*, 1968, 148.