

## Molecular Polarisability. The Conformations of Some Cyclopropyl Ketones

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Dipole moments and molar Kerr constants are reported for the following cyclopropyl ketones examined as solutes in cyclohexane: dicyclopropyl ketone, cyclopropyl methyl ketone, cyclopropyl phenyl ketone, *p*-chlorophenyl cyclopropyl ketone, *p*-bromophenyl cyclopropyl ketone, cyclopropyl *p*-tolyl ketone, and cyclopropyl mesityl ketone. The data are analysed to provide information on the preferred solution-state conformations.

THE ability of the cyclopropyl group to conjugate with adjacent  $\pi$  electron systems has been the subject of many investigations.<sup>1-18</sup> For example, i.r. spectroscopic examination of cyclopropyl ketones has shown that the carbonyl group stretching frequency sensitively reflects the transmission of electron charge from conjugation with and through the cyclopropyl group. From the  $\nu(\text{C}=\text{O})$  values quoted in refs. 6—8, 19, and 20, and those reported in the present work (which are shown in the

Experimental section) we see that the cyclopropyl group as such causes a bathochromic shift in  $\nu(\text{C}=\text{O})$  of the order of  $15\text{ cm}^{-1}$ , approximately half that induced by the phenyl group.

The degree of conjugative interaction in cyclopropyl ketones is dependent on the relative orientations of the carbonyl and cyclopropyl groups and is thought to be maximal for conformations in which the  $\text{C}_3$  and  $\text{C}-\text{CO}-\text{C}$  planes are mutually orthogonal, *i.e.* for the two rotameric forms designated *cis* and *trans* in Figure 1. This is

<sup>1</sup> G. L. Closs and H. B. Klinger, *J. Amer. Chem. Soc.*, 1965, **87**, 3265.

<sup>2</sup> L. V. Vilkov and N. I. Sadova, *Doklady Akad. Nauk S.S.S.R.*, 1965, **162**, 565.

<sup>3</sup> W. A. Bennett, *J. Chem. Educ.*, 1967, **44**, 17.

<sup>4</sup> L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, 1965, **43**, 647.

<sup>5</sup> L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, 1965, **69**, 3043.

<sup>6</sup> J. L. Pierre, R. Barlet, and P. Arnaud, *Spectrochim. Acta*, 1967, **23A**, 2297.

<sup>7</sup> G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Amer. Chem. Soc.*, 1959, **81**, 1660.

<sup>8</sup> M. Hanack, H. Eggensperger, and S. Kang, *Chem. Ber.*, 1963, **96**, 2532.

<sup>9</sup> E. V. Sobolev, V. T. Aleksanyan, Kh. E. Sterin, M. Yu. Lukhina, and L. G. Cherkashina, *Zhur. Strukt. Khim.*, 1961, **2**, 147.

<sup>10</sup> J. L. Pierre, *Ann. Chim.*, 1966, **1**, 383.

<sup>11</sup> D. H. Marr and J. B. Stothers, *Canad. J. Chem.*, 1967, **45**, 225.

<sup>12</sup> H. N. Volltrauer and R. H. Schwendeman, *J. Chem. Phys.*, 1971, **54**, 260 and 268.

<sup>13</sup> E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 1962, 25.

<sup>14</sup> R. H. Eastman and S. K. Freeman, *J. Amer. Chem. Soc.*, 1955, **77**, 6642.

<sup>15</sup> J. P. Pete, *Bull. Soc. chim. France*, 1967, 357.

<sup>16</sup> A. de Meijere and W. Lüttke, *Tetrahedron*, 1969, **25**, 2047.

<sup>17</sup> G. Schrupf, *Tetrahedron Letters*, 1970, 2571.

<sup>18</sup> A. Y. Meyer, B. Muel, and M. Kasha, *Chem. Comm.*, 1972, 401.

<sup>19</sup> R. C. Fuson and F. N. Baumgartner, *J. Amer. Chem. Soc.*, 1948, **70**, 3255.

<sup>20</sup> N. Fuson, M. L. Josien, and E. M. Shelton, *J. Amer. Chem. Soc.*, 1954, **76**, 2526.

in contrast to phenyl ketones wherein  $\pi$  electron delocalisations are greatest for a planar arrangement of the  $C_6$  and CO groupings. In the present work we report

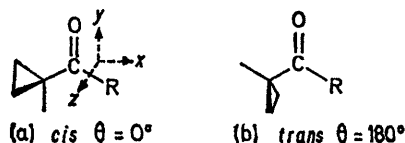


FIGURE 1 *cis*- and *trans*-rotameric forms of cyclopropyl ketones

measurements of the electric dipole moments and molar Kerr constants of a series of cyclopropyl and cyclopropyl phenyl ketones and an analysis of these data to determine the preferred conformations of the molecules examined as solutes in cyclohexane.

## DISCUSSION

**Cyclopropyl Methyl Ketone.**—Standard methods<sup>26,27</sup> were used to calculate theoretical molar Kerr constants for various conformations defined by angles  $\theta$  where  $\theta = 0^\circ$  for the *cis* form shown in Figure 1a and  $180^\circ$  for the *trans* form (Figure 1b). For each geometrical model considered the molecular polarisability tensor components were computed, with reference to the XYZ system of axes shown in Figure 1, using the following component bond and group polarisabilities: \*  $b_L(\text{cyclopropyl}) = b_T(\text{cyclopropyl}) = 5.35$ ,  $b_V(\text{cyclopropyl}) = 3.90$ ;<sup>28</sup>  $b_L(\text{C=O}) = 2.30$ ,  $b_T(\text{C=O}) = 1.40$ ,  $b_V(\text{C=O}) = 0.46$ ;<sup>26</sup>  $b_L(\text{C-C}) = 0.97$ ,  $b_T(\text{C-C}) = b_V(\text{C-C}) = 0.26$ ;<sup>29</sup>  $b_L(\text{C-H}) = b_T(\text{C-H}) = b_V(\text{C-H}) = 0.65$ .<sup>29</sup>

The angles about the carbonyl carbon atom as well as that between the  $C_3$  ring plane and the C-C(carbonyl)

TABLE I

Polarisations, refractions, dipole moments, and molar Kerr constants (from observations on cyclohexane solutions at  $25^\circ$ )

Solute	Concentration range $10^3 w_2$	$\alpha_{\epsilon_1}$ *	$\beta$ *	$\gamma$ *	$\delta$ *	$\infty P_2 / \text{cm}^3$	$R_D / \text{cm}^3$	$\mu / D^\dagger$	$10^{12} \infty (mK_2)^\ddagger$
Dicyclopropyl ketone	1190—4581	6.35	0.167	0.015	-43.1	198	31.9	2.83	-67.5
Cyclopropyl methyl ketone	1224—3538	8.53	0.087	-0.015	26.3	197	24.1	2.90	26.1
Cyclopropyl phenyl ketone	1097—3318	5.07	0.246	0.063	69.8	214	45.4	2.85	134
<i>p</i> -Chlorophenyl cyclopropyl ketone	1394—3047	3.23	0.333	0.060	-10.1	180	50.1	2.49	-27.1
<i>p</i> -Bromophenyl cyclopropyl ketone	1353—4122	2.67	0.457	0.061	-21.5	184	53.5	2.48	-74.7
Cyclopropyl <i>p</i> -tolyl ketone	702—2441	5.29	0.230	0.064	117	244	50.6	3.05	250
Cyclopropyl mestyl ketone	940—3021	3.61	0.194	0.055	-123	213	60.1	2.71	-315

\* Incremental changes in the dielectric constants, densities, refractive indices, and Kerr constants ( $\Delta\epsilon$ ,  $\Delta d$ ,  $\Delta n$ , and  $\Delta B$ , respectively) were measured for solutions having solute weight fractions  $w_2$ . The coefficients,  $\alpha_{\epsilon_1}$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  were derived from the relations:  $\alpha_{\epsilon_1} = \Sigma \Delta\epsilon / \Sigma w_2$ ;  $\beta = \Sigma \Delta d / d_1 \Sigma w_2$ ;  $\gamma = \Sigma \Delta n / n_1 \Sigma w_2$ ;  $\delta = \Sigma \Delta B / B_1 \Sigma w_2$ .  $^\dagger$  Calculated on the basis that  $n_D P = 1.05 R_D$ .

$^\ddagger$  The term  $\infty (mK_2)$  refers to the solute molar Kerr constant at infinite dilution.

## EXPERIMENTAL

**Materials, Apparatus, etc.**—Dicyclopropyl ketone, cyclopropyl methyl ketone, and cyclopropyl phenyl ketone were commercial samples which were distilled immediately before use to give b.p. 162—163, 111, and 97—100° at ca. 4 mmHg, respectively. The other solutes were prepared by the method of Close<sup>21</sup> and were purified to give *p*-chlorophenyl cyclopropyl ketone, b.p. 113—115° at ca. 0.5 mmHg, *p*-bromophenyl cyclopropyl ketone, b.p. 108—109° at ca. 1.2 mmHg, cyclopropyl *p*-tolyl ketone, m.p. 48—50° (from light petroleum), and cyclopropyl mesityl ketone, b.p. 97—101° at ca. 1.0 mmHg. The i.r. spectrum of each compound was recorded using a Perkin-Elmer 457 spectrometer; all were examined as pure liquids except for cyclopropyl *p*-tolyl ketone which was measured in Nujol. The  $\nu(\text{C=O})$  stretching frequencies are, in turn, 1683, 1696, 1664, 1666, 1666, 1673, and 1680  $\text{cm}^{-1}$ . The following constants apply at  $25^\circ$  for cyclohexane (dried over sodium):  $\epsilon_1 = 2.0199$ ;  $d_1 = 0.77389$ ;  $(n_1)_D = 1.4235$ ;  $10^7(B_1)_D = 0.054$ ;  $10^{14}(sK_1) = 1.35$ . Apparatus, techniques, symbols used, and methods of calculation have been described before.<sup>22-25</sup> The experimental results are summarised in Table 1.

\* The polarisability semi-axes of bonds and groups  $b_L$ ,  $b_T$ , or  $b_V$  are quoted throughout in  $\text{\AA}^3$  units.

<sup>21</sup> W. J. Close, *J. Amer. Chem. Soc.*, **1957**, **79**, 1455.

<sup>22</sup> C. G. Le Fèvre and R. J. W. Le Fèvre, *Rev. Pure Appl. Chem.*, **1955**, **5**, 261.

<sup>23</sup> R. J. W. Le Fèvre, 'Dipole Moments,' Methuen, London, 3rd edn., 1953.

<sup>24</sup> C. G. Le Fèvre and R. J. W. Le Fèvre, in 'Physical Methods of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 3rd edn., 1960, vol. 1, ch. XXXVI, p. 2459.

bond axis were taken as  $120^\circ$ .<sup>5</sup> Small changes in the angles do not significantly affect the calculations. The experimental molecular refraction exceeds that calculated from bond and group refractivities<sup>30</sup> by 0.1  $\text{cm}^3$  and this corresponds to a small polarisability exaltation of  $+0.1_2$  which we regard as a correction to the C-C (carbonyl) longitudinal polarisability because of conjugation effects.<sup>26</sup> The precise direction of action of the permanent electric moment is difficult to specify. The dominant polar group is the carbonyl and calculations were made assuming that  $\mu(\text{cyclopropyl methyl ketone})$  is coincident with the C=O bond axis. The  $mK(\text{calc.})$  values so obtained when plotted against  $\theta$  result in the curve (unbroken) shown in Figure 2. Comparison of the experimental molar Kerr constant ( $26.1 \times 10^{-12}$ ) with the theoretical values indicates that the molecule exists completely as the *cis*-form. This result is in accord with the microwave data of Lee<sup>31</sup> who found no evidence for any species other than the *cis*. If, how-

<sup>25</sup> R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, **1963**, 4933.

<sup>26</sup> R. J. W. Le Fèvre, *Adv. Phys. Org. Chem.*, **1965**, **3**, 1.

<sup>27</sup> J. M. Eckert and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1962**, 1081.

<sup>28</sup> M. J. Aroney, R. J. W. Le Fèvre, W. Lüttke, G. L. D. Ritchie, and P. J. Stiles, *Austral. J. Chem.*, **1963**, **21**, 2551.

<sup>29</sup> R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, **1966**, 273.

<sup>30</sup> A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, **1952**, 514.

<sup>31</sup> P. L. S. Lee, *Diss. Abs. Int. B*, **1972**, **32**, 5131.

ever, the molecular moment is not exactly coincident with the C=O axis but is inclined *e.g.* 5° to that axis (*cf.* acetophenone wherein  $\mu$  is *ca.* 10° away from C=O<sup>32</sup>) then the graph of  ${}_mK(\text{calc.})$  against  $\theta$  is represented by

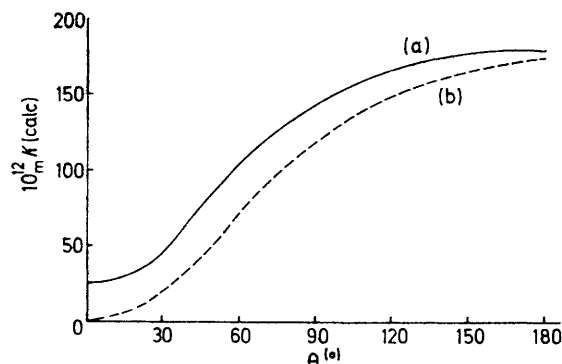


FIGURE 2 Plot of  ${}_mK(\text{calc.})$  against  $\theta$  for (a)  $\mu(\text{cyclopropyl methyl ketone})$  coincident with the C=O axis and (b) inclined at 5° to it

the broken line of Figure 2. This results in a 93% contribution of *cis*-form within a *cis-trans*-conformational equilibrium (*cf.* Bartell *et al.*<sup>5</sup> who proposed, from electron diffraction, a *cis:trans*-ratio of  $80 \pm 15 : 20 \pm 15$ ). We conclude that cyclopropyl methyl ketone exists in cyclohexane solution predominantly (>90%) as the *cis*-form and with a minor (<10%) *trans*-component.

**Dicyclopopyl Ketone.**—The *cis-cis*-model in which each cyclopropyl group is *cis* to the carbonyl link is shown in Figure 3. The molar Kerr constant was calcu-

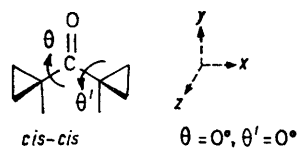


FIGURE 3 *cis-cis*-Model of dicyclopopyl ketone

lated for this conformer on the basis that the measured moment is located along the C=O axis and the polarisability exaltation ( $\Delta b = 0.34$ ) is equally apportioned along each of the two C(cyclopropyl)-C(carbonyl) longitudinal axes. The theoretical  ${}_mK$  is  $-58 \times 10^{-12}$ , *i.e.* close to the observed ( ${}_mK_2$ ) of  $-67.5 \times 10^{-12}$ . Other conformations generated from this model by rotations of one or both cyclopropyl groups away from a *cis*-disposition, lead to calculated molar Kerr constants which are greater (more positive) than for the *cis-cis*-form. For example,  ${}_mK(\text{calc.})$  for conformer  $\theta = 90^\circ$ ,  $\theta' = 90^\circ$  (antisymmetric rotations) is  $161 \times 10^{-12}$  while  $180^\circ$  rotations leading to the *trans-trans*-form result in a predicted  ${}_mK$  of  $230 \times 10^{-12}$ . Dicyclopopyl ketone as a solute clearly exists virtually completely as the *cis-cis*-form.

**Cyclopropyl Phenyl Ketone and Cyclopropyl p-Substituted Phenyl Ketones.**—The following additional group polarisability data are required for the analysis of the

molar Kerr constants of the molecules  $p\text{-XC}_6\text{H}_4\text{COC}_3\text{H}_5$  where X is H, Cl, Br, or Me:  $b_L(\text{Ph}) = b_T(\text{Ph}) = 10.50$ ,  $b_V(\text{Ph}) = 6.79$ ;<sup>33</sup>  $b_L(\text{C}_{\text{ar}}\text{-Cl}) = 4.20$ ,  $b_T(\text{C}_{\text{ar}}\text{-Cl}) = 1.95$ ,  $b_V(\text{C}_{\text{ar}}\text{-Cl}) = 1.50$ ;<sup>26</sup>  $b_L(\text{C}_{\text{ar}}\text{-Br}) = 6.20$ ,  $b_T(\text{C}_{\text{ar}}\text{-Br}) = 2.40$ ,  $b_V(\text{C}_{\text{ar}}\text{-Br}) = 2.20$ ;<sup>26</sup>  $b_L(\text{C}_{\text{ar}}\text{-Me}) = 3.55$ ,  $b_T(\text{C}_{\text{ar}}\text{-Me}) = 1.90$ ,  $b_V(\text{C}_{\text{ar}}\text{-Me}) = 2.31$ .<sup>33</sup> The direction of action of the electric moment for each solute was obtained vectorially by regarding  $\mu(\text{res.})$  as the vector sum of the components  $\mu_1$  and  $\mu_2$  in Figure 4 where  $\mu_1 (= 2.85 \text{ D})$  is the moment of cyclopropyl phenyl ketone (which is taken along C=O) and  $\mu_2$  is composed of  $\mu(\text{C}_{\text{ar}}\text{-X})$  and the 'interaction moment' between the 1 and 4 substituents on the phenyl group. The values calculated for  $\mu_2$  are:  $+1.76$ ,  $+1.66$ , and  $-0.37 \text{ D}$  for X = Cl, Br, and Me, respectively. Polarizability exaltations  $\Delta b$  were obtained in each case from  $\Delta_E P = 0.95 \Delta R_D$  where  $\Delta R_D = R_D(\text{obs.}) - R_D$  (calculated by additivity<sup>30</sup> of component bond and group refractions). After allowing for the

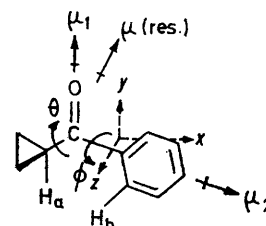


FIGURE 4 Estimation of  $\mu(\text{res.})$  for cyclopropyl *p*-substituted phenyl ketones

C(cyclopropyl)-C(carbonyl) longitudinal polarisability correction ( $0.12$ ) found earlier, the residual  $\Delta b$  was added to the  $b_L$  of the C(aromatic)-C(carbonyl) bond to correct for phenyl-carbonyl conjugative interactions.<sup>26</sup> Theoretical molar Kerr constants were calculated for various conformational models specified by angles of twist  $\theta$  of the cyclopropyl group and  $\phi$  of the phenyl ring. As before,  $\theta = 0^\circ$  for a *cis*-disposition of  $\text{C}_3\text{H}_5$  with C=O. The angle  $\phi$  is  $0^\circ$  when the aromatic  $\text{C}_6$  group is coplanar with C=O. Only antisymmetric rotations have been considered to minimise steric interactions between  $\text{H}_a$  and  $\text{H}_b$  (see Figure 4). The calculations are summarised in Table 2.

The experimental molar Kerr constants for the molecules  $p\text{-XC}_6\text{H}_4\text{COC}_3\text{H}_5$  are  $134 \times 10^{-12}$  (X = H),  $-27.1 \times 10^{-12}$  (X = Cl),  $-74.7 \times 10^{-12}$  (X = Br), and  $250 \times 10^{-12}$  (X = Me), respectively. Comparison with the calculated values shows clearly that for each of the four compounds in this group the preferred solution-state conformation is one defined by  $\theta = 25 \pm 5^\circ$  and  $\phi = 25 \pm 5^\circ$ . No other combination of  $\theta$  and  $\phi$  values yields accord between experiment and calculation simultaneously for all four molecules. Examination of scale models indicates that the conformation ( $\theta = 25^\circ$ ,  $\phi = 25^\circ$ ) is a sterically acceptable form of the molecule in each case;  $|\theta + \phi|$  values of *ca.*  $40^\circ$  or less introduce steric interaction between the cyclopropyl group and the *ortho*-hydrogen atoms of the aromatic ring. Further, twists of only *ca.*  $25^\circ$  in  $\theta$  and  $\phi$  do not greatly inhibit the

<sup>32</sup> J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 1949, 2957.

<sup>33</sup> R. J. W. Le Fèvre and L. Radom, *J. Chem. Soc. (B)*, 1967, 1295.

TABLE 2

Calculated molar Kerr constants for conformations of cyclopropyl phenyl ketone and cyclopropyl *p*-substituted phenyl ketones

Solute	$\theta$	$\phi$	$10^{12} {}_mK(\text{calc.})$
Cyclopropyl phenyl ketone	0	0	189
	30	0	208
	60	0	256
	90	0	303
	180	0	331
	0	30	92
	0	90	-193
	25	25	139
<i>p</i> -Chlorophenyl cyclopropyl ketone	180	90	-49
	0	0	38
	90	0	91
	0	30	-68
<i>p</i> -Bromophenyl cyclopropyl ketone	25	25	-31
	0	0	-29
Cyclopropyl <i>p</i> -tolyl ketone	25	25	-75
	0	0	202
	0	30	170
	30	19	250

ability of either the phenyl or the cyclopropyl groups to conjugate with the carbonyl  $\pi$  electron system.

*Cyclopropyl Mesityl Ketone.*—The experimental molar Kerr constant is large and negative ( $-315 \times 10^{-12}$ ) indicating, from the Langevin-Born theory,<sup>22</sup> that the molecular moment vector must be inclined close ( $<30^\circ$ ) to the minimum polarisability axis of the molecule which

in turn is near perpendicular to the aromatic ring plane of the highly anisotropic mesityl group. Calculations were made using  $b_L(\text{mesityl}) = b_T(\text{mesityl}) = 16.49$ ,  $b_V(\text{mesityl}) = 11.68$ ,<sup>34</sup> and  $\Delta b = 1.77$ . The hypothetical form  $\theta = 0^\circ$ ,  $\phi = 0^\circ$  (which is sterically impossible) has an algebraically positive theoretical  ${}_mK$  since  $\mu$  lies in the plane of the highly polarisable mesityl group. If  $\mu$  is taken to act along the carbonyl bond axis the  ${}_mK(\text{calc.})$  value for this conformer is  $227 \times 10^{-12}$ .

Rotating  $\theta$  from  $0^\circ$  leads to a greater, positive  ${}_mK$ . As  $\phi$  increases from 0 to  $90^\circ$  the theoretical molar Kerr constant becomes more negative and an optimal negative value of  $-217 \times 10^{-12}$  is attained when  $\theta = 0^\circ$ ,  $\phi = 90^\circ$ . The experimental  ${}_mK$  is more negative ( $-315 \times 10^{-12}$ ); however, calculations show that for this conformation small variations in the location assumed for  $\mu$  very sensitively affect the calculated Kerr constant. The theoretical  ${}_mK$  for this rotamer is in accord with the observed  $\infty({}_mK_2)$  if  $\mu$  is directed  $8^\circ$  away from the carbonyl longitudinal axis so that it makes an angle of  $22^\circ$  with the normal to the aromatic ring plane.

The award of a Commonwealth Postgraduate Studentship to H. J. S. and support from the Australian Research Grants Committee are gratefully acknowledged.

[3/285 Received, 8th February, 1973]

<sup>34</sup> P. H. Gore, J. A. Hoskins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, 1969, 485.