

**189.** *Refractive Indices and Molecular Refractivities of  
3-Methylcyclohexanone and Pulegone.*

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Refractive indices over a wide range of wave-lengths in the visible and the ultra-violet region, including those covered by the ketonic absorption band at about 3000  $\mu$ , are recorded for pulegone and for 3-methylcyclohexanone. The refractivities of the carbonyl radical in each compound are deduced and compared with those previously recorded for this radical in cyclohexanone. An enhanced molecular refractivity in pulegone, which might be described as an "optical exaltation" in view of the conjugation of carbonyl and ethylenic double bonds, cannot be attributed to the presence of an absorption band which does not appear in the spectra of the other compounds, since equally abnormal values are obtained for 3-methylcyclohexanone, to which this explanation cannot be applied. It is concluded that these effects result from the invalidity of the additive relationship in the presence of strongly chromophoric radicals, as predicted in a previous paper.



The molecular refractivities,  $M(n^2 - 1)/d(n^2 + 2)$ , at  $\lambda = 5896 \text{ \AA}$ , together with that of *cyclohexanone* (Allsopp, *Proc. Roy. Soc.*, 1934, A, 146, 300) and the values calculated from Eisenlohr's standard atomic refractivities ("Spectrochemie Organischer Verbindungen," 1912, p. 94), are shown in Table II. That for *pulegone* is 0.52 unit higher than the

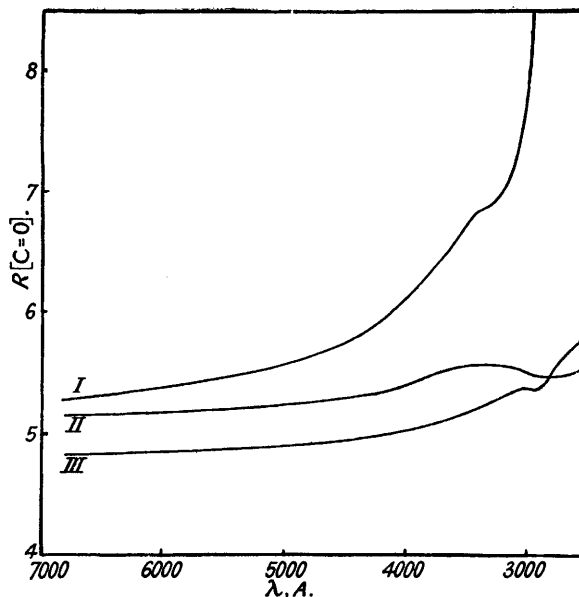
TABLE II.

Molecular Refractivities at  $\lambda = 5896 \text{ \AA}$ .

	$R$ (obs.).	$R$ (calc.).	Obs.—Calc.
<i>cyclohexanone</i> .....	27.93	27.72	0.21
3-Methyl <i>cyclohexanone</i> .....	32.88	32.34	0.54
<i>Pulegone</i> .....	46.24	45.72	0.52

calculated value and could be described as an "optical exaltation" due to the conjugation of ethylenic and carbonyl double bonds (Brühl, *Ber.*, 1907, 40, 878, 1153) but for the

FIG. 2.

Refractivity of the carbonyl radical in *pulegone*, I, 3-methyl*cyclohexanone*, II, and in *cyclohexanone*, III.

observation, recorded in the table, that 3-methyl*cyclohexanone*, with no such structural complication, gives rise to an even larger excess, *viz.*, 0.54 unit; and the refractivity of the still simpler molecule of *cyclohexanone* is also not normal.

An attempt was made to account for the anomalies by "dissecting out" the refractivity of the carbonyl radical alone, over the whole range of wave-lengths covered by the present measurements. For this purpose, use was made of the refractivities of methylene (Allsopp and Willis, *Proc. Roy. Soc.*, 1936, A, 153, 379) and of *cyclohexene* (Allsopp, *ibid.*, 1934, A, 143, 618), the latter containing the correction necessary in the presence of an ethylenic double bond. Thus:

$$R(\text{C}=\text{O})_{\text{C}_{10}\text{H}_{16}\text{O}} = R(\text{C}_{10}\text{H}_{16}\text{O}) - R(\text{C}_6\text{H}_{10}) - 3R(\text{CH}_2)$$

$$R(\text{C}=\text{O})_{\text{C}_7\text{H}_{12}\text{O}} = R(\text{C}_7\text{H}_{12}\text{O}) - 6R(\text{CH}_2)$$

The results are shown in Fig. 2, together with values of  $R(\text{C}=\text{O})$  derived from *cyclohexanone* (Lowry and Allsopp, *ibid.*, 1934, A, 146, 313). Curves II, obtained from methyl*cyclohexanone*, and III, from *cyclohexanone*, have a uniform separation until they reach the ketonic bands (the maxima of which do not coincide in the two compounds); but they then converge and actually intersect at about 2750  $\text{\AA}$ . The initial separation is similar in

magnitude to that between curve II and curve I, from pulegone, which should represent the optical exaltation.

Curves I and II diverge rapidly, as is to be expected, when the former approaches the wave-length of the absorption band at 2450 Å. A careful analysis of the curves of refractive dispersion by means of Ketteler-Helmholtz equations showed, however, that the contribution of this band to the refractive indices at long wave-lengths is numerically *less* than that made by the 1900 Å. band to the indices of methylcyclohexanone, and that the band at 1900 Å. makes little or no contribution in the case of pulegone. It is therefore not possible to explain the enhanced refractivities in terms of the position and relative intensities of the ultra-violet absorption bands (cf. Lowry and Allsopp, *ibid.*, 1937, A, 163, 356); and it must be concluded that the "atomic" refractivity of the carbonyl radical is not constant, irrespective of the state of substitution or unsaturation of the molecule in which it is located. This result is in accordance with the conclusion reached by Allsopp and Willis (*ibid.*, 1936, A, 153, 392) that additivity of atomic refractivities can only be expected to occur for those molecules whose absorption spectra contain no strong absorption bands in the accessible ultra-violet. It follows that the enhanced refractivities which are often (but not always) associated with conjugated systems must not be given all the significance which was attributed to them by Brühl, but may be due to the fundamental invalidity of an essentially empirical additive relationship.

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