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STRUCTURE AND REACTIVITY OF CYCLOPROPENONES III 1)

ASSIGNMENT OF INFRARED AND RAMAN BANDS IN CYCLOPROPENONES

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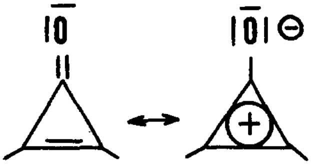
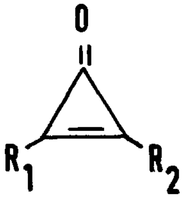
The assignment of the two very strong characteristic bands at 1840-1865 and 1600-1660 cm^{-1} in the IR spectra of cyclopropenones (1a, 1b) has been controversial 1-7). The recent publication of three papers 4-6), in which the band near 1645 cm^{-1} in diphenylcyclopropenone (2) has been either assigned to the C=O stretching mode 4,6) or considered to have predominantly C=O character 5) prompts us to summarize our results and conclusions and to report some new findings in this area:

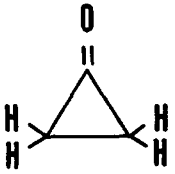


1a 1b



2: $R_1=R_2=C_6H_5$ 4: $R_1=CH_3;R_2=H$

3: $R_1=R_2=CH_3$ 5: $R_1=n\text{-}C_3H_7$; $R_2=H$



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1) Application of the solvent variation technique 8) to 2 1-7) and several dialkylcyclopropenones 1,3,7) has shown that the band near 1640 cm^{-1} is shifted much more to lower wavenumbers in solvents of increasing polarity

than the other strong band. Thus, the behaviour of the 1640 cm^{-1} band parallels that of most other ketones 8) and on these grounds this band has been assigned to the C=O stretching frequency 4-7). However, strong coupling is to be expected in very rigid ring systems 9), such as cyclopropenones, and in a strongly coupled system the response of an observed band to solvent change will differ from that of an essentially localized mode and will not be simple 10). Moreover, the band at 1817 cm^{-1} in the related cyclopropanone (**6**) which is assigned to a C=O stretching mode is shifted to *higher* wavenumbers in solvents of increasing polarity in contrast to all solvent shifts observed so far in other carbonyl compounds 11). For these reasons, in our opinion the solvent variation results cannot be used for an assignment of the bands in cyclopropenones. We have explained the observed solvent dependence in the following way: In more polar solvents the contribution of the dipolar form **1b** is enhanced which would lead to a shift of both hypothetically uncoupled group vibrations to *lower* wavenumbers. However, as a result of the increased bond order of the connecting C-C ring bonds in **1b**, coupling and consequently coupling repellence is increased. This causes a larger shift to *higher* wavenumbers in the 1850 cm^{-1} band and to *lower* wavenumbers in the 1640 cm^{-1} band. Thus, in the 1850 cm^{-1} band both effects almost cancel each other, whereas in the 1640 cm^{-1} band they add 3). The occurrence of strong coupling in cyclopropenones is based on the following evidence:

2) O^{18} substitution in **3** affects several bands in the IR and Raman spectra; the bands near 1840 cm^{-1} ($\Delta\nu$ = 13 cm^{-1}), 1640 (12), 1120 (10) and 890 cm^{-1} (11) are shifted to lower wavenumbers significantly, other bands are displaced by about 3 cm^{-1} 2). In O^{18} substituted **2** both strong bands are shifted, but the band near 1850 cm^{-1} to a larger extent ($\Delta\nu$ = 14-21 cm^{-1} depending on the solvent) 1). The effect of O^{18} substitution on several bands and the relatively small shift on O^{18} substitution - the shift in normal ketones is about 30 cm^{-1} 12) - can only be explained by strong mixing of several modes.

3) In the Raman spectra of the cyclopropenones the band near 1640 cm^{-1} is by far the most intense band 1,3); a pure C=O stretching mode should not be so strong.

4) The position of both strong cyclopropenone bands in methylcyclopropenone (4) and propylcyclopropenone (5) are displaced to lower wavenumbers compared to the corresponding symmetrically disubstituted compounds, but the band near 1640 cm^{-1} is shifted by about 50 cm^{-1} and the 1850 cm^{-1} band only by 10-20 cm^{-1} 13). Again, if the 1640 cm^{-1} band were a pure C=O stretching mode, the large (50 cm^{-1}) shift could not be explained, since no change takes place in the relative mass and geometry of the atoms participating in a pure C=O stretching vibration. The observed substituent influence is in accord with the results of the normal coordinate analysis (see below); these show that the νC-R coordinates in 2 and 3 participate in the 1640 cm^{-1} band to about 15 %, but in the 1850 cm^{-1} band only to about 5 % 2).

5) A normal coordinate analysis using a modified valence force field has been carried out for 2 and 3. According to calculations the potential energy of the vibrations is distributed as follows: 1850 cm^{-1}: 40-50 % on C=O, 10-20 % on C=C and 30-35 % on C-C (ring); 1640 cm^{-1}: 20-30 % on C=O, 55-60 % on C=C and about 0 % on C-C (ring). A third vibration, at 880 cm^{-1} in the Raman spectrum, is distributed over the same bonds: 15-20 % on C=O, about 15 % on C=C and 55-65 % on C-C (ring). The calculated eigenvectors show that in the 1850 cm^{-1} band the phase of the C=O group is opposite to that of the bonds in the ring, whereas in the 1640 cm^{-1} mode the C=O and the C=C group are vibrating in phase 2).

As a conclusion from all results, the 1850 cm^{-1} band can be assigned to an out of phase stretching vibration of the two double bonds with a predominance of the C=O coordinate and the 1640 cm^{-1} band to the corresponding in phase stretching vibration with a predominance of the C=C coordinate. The band at 880 cm^{-1} is mainly a symmetric stretching vibration of the C-C bonds in the ring. All three vibrations must be considered as typical features of the cyclopropenone system.

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