108.   *The Infra-red Spectrum of Tropolone.*

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The infra-red absorption spectrum of a pure synthetic sample of tropolone has been recorded in the region 3800—650 cm.$^{-1}$ and compared with measurements on certain closely allied synthetic and natural derivatives as well as with relevant data on other related organic structures. Tentative empirical assignments of some of the observed vibration frequencies have been made.

Considerations based on the characteristic OH absorption lead to a tropolone structural model in which the existence of two equivalent energy minima for the location of a highly mobile tautomeric hydrogen is recognised. Infra-red spectrometry may be employed to diagnose the presence or otherwise of the tropolone nucleus in a complex organic structure.

In a complex unsymmetrical molecule such as tropolone (I), nothing like a complete assignment of observed vibration frequencies to specific modes of vibration can be attempted, and no rigorous determination of bond-force constants or molecular geometry can therefore be made. It is well known, however, that the stretching vibration of certain special bonds in a polyatomic molecule may take place almost independently of the rest of the molecule and may very nearly involve the restoring force constant of only that bond. The O–H linkage represents such a special bond *par excellence*, and its nature in a given molecule can therefore be investigated by infra-red absorption technique. From the point of view of tropolone structure, this is fortunate, in that the nature of its hydroxyl bond happens to be a critical feature of the structure as a whole.

The O–H Region and its Structural Significance.—In dilute solution in a non-polar solvent, no sharp band near 3600 cm.$^{-1}$ characteristic of similar dilute solutions of simple alcohols or phenols could be observed for tropolone. Instead, there appeared a very broad region of moderate intensity around 3100 cm.$^{-1}$. Similar bands at 3200 cm.$^{-1}$ have been reported by Scott and Tarbell (*J. Amer. Chem. Soc.*, 1950, **72**, 240) for colchiceine and thujaplicin, two naturally occurring derivatives. These results specify rather strong intramolecular association of the hydroxyl group in tropolone, doubtless involving a hydrogen bond with the neighbouring carbonyl-oxygen. The breadth and relatively low intensity of the band are just like those found in a typical β-diketone enol such as acetylacetone (IV), although its frequency position is significantly lower in the latter, at 2700 cm.$^{-1}$ (Rasmussen, Tunnicliff, and Brattain, *ibid.*, 1949, **71**, 1068). This difference indicates appreciably greater strength of internal association in the β-diketones than in tropolones, as would be expected from the sterically much more favourable conditions for hydrogen-bond formation in a six- as against a five-membered ring. It is not possible to calculate the energy (ΔH) of a hydrogen bond from frequency data alone, but spectroscopic comparison with the dimeric carboxylic acids (in which this energy is known from equilibrium studies and gives rise to a broad band around 3000 cm.$^{-1}$) suggests that a figure of ∼7 kcals. will be of the right order of magnitude for tropolone. The length of the bond may also be roughly estimated by application of one or other of the approximations relating vibration frequency or force constant to bond length (*e.g.*, Badger, *J. Chem. Physics*, 1934, **2**, 128). It then appears that the frequency shift of the hydroxyl band from its normal " unassociated " position ($-\Delta \nu / \nu$ ∼14%) must lead to a lengthening of the normal covalent OH bond distance of 0·98 Å. to not more than 1·1 Å. in tropolone. Scale models immediately reveal that this estimate precludes anything like a symmetrical equilibrium position of the proton between the two oxygen atoms in the structure. Depending on the precise choice of the other molecular parameters involved (particularly the uncertain CCO and COH angles), we find that the hydroxylic hydrogen is still some 1·5—2·0 Å. distant from the carbonyl oxygen with which it is associated. The possibility of electronic resonance degeneracy involving two equivalent bonds between the proton and the two oxygen atoms is therefore ruled out by spectroscopic evidence.

Now, it is known from infra-red data that only *weak* internal hydrogen-bond formation through a five-membered ring arises in the geometrically analogous structures of 2-hydroxy-*cyclo*hexanone (Sheehan, O'Neill, and White, *J. Amer. Chem. Soc.*, 1950, **72**, 3376) or catechol (Wulf and Liddel, *ibid.*, 1935, **57**, 1464). *Strong* hydrogen bonding such as that observed in tropolone can only take place when the donor–acceptor properties of either or both of the

oxygen and hydrogen atoms involved in the bond have been greatly enhanced by some additional structural condition. We are therefore compelled to postulate important resonance contributions from ionic structures such as (I*a*), carrying a formal negative charge on the carbonyl oxygen and a simultaneous increase in the acceptor properties of the proton (cf. Rasmussen *et al., loc. cit.*). Such resonance, of course, implies a " smearing out " of alternate single and double bonds in the presumably planar seven-membered ring. On this geometrical basis, our tropolone model is seen to be related to its tautomeric mirror-image form (II) and (II*a*) by little change other than a " jump " of the proton through some 0·5—1·0 A. A comparable separation of two mirror-image forms has been found to exist in the ammonia molecule (Dennison and Uhlenbeck, *Physical Rev.*, 1932, **39**, 938) and the bifluoride ion (Ketelaar, *Rec. Trav. chim.*, 1941, **60**, 523) where it leads to protonic oscillation between the two equivalent energy minima. Such oscillation is slow compared with the vibration period of the X–H bond and does not confer appreciable additional resonance energy on the structure, but it is extremely rapid from the point of view of tautomeric interconversion. We may, therefore, expect the hydroxylic hydrogen atom of tropolone to be symmetrically located *on a time average basis* between the two oxygen atoms which will thus become chemically indistinguishable, at least in the absence of unsymmetrical nuclear substitution.
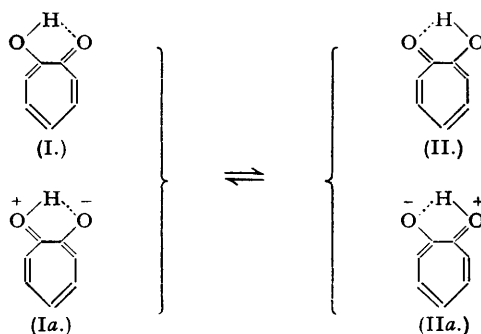
The tropolone model resulting from the above discussion based on infra-red absorption data seems to substantiate the modified suggestions made by Dewar (*Nature*, 1945, **155**, 479). Its stabilization energy will correspond approximately to the energy of the hydrogen bond (∼7 kcals.) together with the resonance energy of four conjugated double bonds (∼17 kcals.; Pauling, *Helv. Chim. Acta*, 1949, **32**, 2241) and the further conjugation of a hydroxyl group (∼7 kcals.), totalling about 31 kcals. This stabilization will be diminished by a few kcals. arising from steric strain in the seven-membered ring, and thus accords quite satisfactorily with the experimental thermochemical value of 28·6 kcals. (see preceding paper). Although the apparently close numerical agreement may be fortuitous in view of the many approximations involved, it serves independently to illustrate the energetic plausibility of our structural deductions.

The C–H Region.—In the C–H bond stretching vibrations of organic molecules, mechanical coupling often occurs with a resultant splitting of vibrational levels, but the average location of the characteristic absorption near 3000 cm.$^{-1}$ affords some measure of the force constant of such bonds. Unfortunately, this region is partly masked in tropolone by overlapping of the broad OH band and may be further obscured by overtone frequencies of the very intense bands near 1500 cm.$^{-1}$ (see below). The small peaks at 3050 and 3015 cm.$^{-1}$, however, appear to be genuine C–H fundamentals since they could also be observed in the copper derivative of tropolone where OH absorption is, of course, absent and where the 1500 cm.$^{-1}$ region is appreciably different. Their location seems in agreement with that for an unsaturated or aromatic molecule (Fox and Martin, *Proc. Roy. Soc.*, 1940, *A*, **175**, 208), but may be slightly affected by steric strain (see below).

The C=O Region.—An impressive mass of evidence has accumulated during the last few years, demonstrating that the carbonyl group in an organic molecule invariably appears to give rise to a characteristic single intense absorption band in the region 1800—1600 cm.$^{-1}$, whatever the other groups attached to the same or adjoining carbon atoms in the molecule and whether or not hydrogen-bond formation occurs (cf. *e.g.*, Hartwell, Richards, and Thompson, *J.*, 1948, 1436; Rasmussen *et al., loc. cit.*, and *ibid.*, p. 1073; Blout, Fields, and Karplus, *J. Amer.*

Chem. Soc., 1948, **70**, 194; Flett, *J.*, 1948, 1441). Moreover, the actual position of the band in this frequency range generally affords a qualitative indication of the force constant or bond order of the carbonyl group involved. Accordingly, Scott and Tarbell (*loc. cit.*) assumed that the first intense infra-red absorption of several naturally occurring tropolones and derivatives near 1620 cm.$^{-1}$ must be associated with the carbonyl group, and they discussed the possible effects of conjugation or hydrogen bonding in connection with the location of the frequency near this lower limit of its normal range.

Tropolone itself exhibits the same intense absorption at 1615 cm.$^{-1}$. Assuming the reasonable but by no means proven premise that the frequency does arise from an approximately independent vibration of the carbonyl bond, we believe that three factors, *viz.*, conjugation, hydrogen bonding, and steric strain, may be jointly responsible for the low force constant involved, but that it is impossible to evaluate the relative importance of these effects on existing evidence. Scott and Tarbell's observation of an unchanged "carbonyl" frequency in a tropolone methyl ether (colchicine) does not necessarily exclude the hydrogen-bonding effect : the structure of *O*-methyltropolones may well involve enhanced stability of the ionic resonance form, promoting internal hydrogen-bond formation between the carbonyl and methyl groups in a sterically favourable six-membered ring (III*a*). Steric strain is expected to lower the carbonyl force constant on the following grounds. In five-membered cyclic carbonyl compounds

(III*a*)

(IV.)

in which ring strain is of opposite sign to that expected in the seven-membered planar tropolone ring, the frequency is invariably *higher* than that of the strainless six-membered ring analogues (Hartwell *et al.*, *loc. cit.*; Jones, Williams, Whalen, and Dobriner, *J. Amer. Chem. Soc.*, 1948, **70**, 2024; Woodward, *ibid.*, 1950, **72**, 3327). This peculiarity seems to be part of a quite general phenomenon (Kohlrausch *et al.*, *Ber.*, 1936, **69**, 729; Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 1; Plyler and Acquista, *J. Res. Nat. Bur. Stand.*, 1949, **43**, 37; Goubeau, *Annalen*, 1950, **567**, 214) which has a theoretical basis in $s : p$ hybridization ratio changes of the carbon σ valency orbitals (Coulson and Moffitt, *loc. cit.*) : all bonds directly attached to a small strained ring become stronger, whereas the bonds forming part of the ring are weakened. In tropolone, the reverse effects should occur since angular strain would here be relieved by an increase rather than decrease of the normal (trigonal) $s : p$ hybridization ratio of the σ valencies in the ring, resulting in a corresponding decrease of the same ratio in the σ orbitals forming the bonds attached to the ring. These changes would lead to a weakening of the carbonyl bond. Insufficient critical data are available to estimate the importance of such an effect in tropolone, but the low vibration frequency (1640 cm.$^{-1}$) of the carbonyl bond in the undoubtedly planar and possibly even more highly strained 4· : 5-benzo*cyclo*hepta-2 : 6-dienone (Scott and Tarbell, *loc. cit.*; Volpin and Plate, *Chem. Abs.*, 1950, **44**, 6846) suggests its real existence in a comparable molecule.

In the crystals or in chloroform solutions of the copper derivative of tropolone, the 1615-cm.$^{-1}$ frequency has been lowered beyond what might be ascribed to a solvent effect to 1590 or 1595 cm.$^{-1}$, respectively. This further decrease may be associated with the secondary co-ordination bond between the carbonyl group and the metal.

The Long-wave Region, 1600—650 *cm.*$^{-1}$.—Beyond the presumed carbonyl frequency at 1615 cm.$^{-1}$, tropolone exhibits an intense band at 1553 cm.$^{-1}$ and other intense and complex absorption at about 1475, 1440, 1255, and 720 cm.$^{-1}$, apart from the smaller and less characteristic bands shown in the figure. Accumulated structure correlation evidence from other organic compounds (*e.g.*, Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397) suggests that the 1553-cm.$^{-1}$ band and some at least of the 1500—1400-cm.$^{-1}$ absorption may be associated with in-plane vibrations of the carbon ring, that the 1500—1400-cm.$^{-1}$ region will also contain C–H deformation frequencies, that the complex 1255-cm.$^{-1}$ structure is due to both C–O single bond stretching and O–H deformation vibrations, and that the intense doublet at 720 cm.$^{-1}$ is associated with out-of-plane vibrational modes of the nuclear hydrogen atoms. In the crystalline copper derivative, the 720-cm.$^{-1}$ structure remained almost unchanged, the 1255-cm.$^{-1}$ region was centred at 1230 cm.$^{-1}$, the 1553-cm.$^{-1}$ frequency had apparently been lowered to 1518 cm.$^{-1}$ (1517 cm.$^{-1}$ in chloroform solution), and instead of the broad absorptions in the

1500—1400-cm.$^{-1}$ region there now appeared two narrow bands at 1414 and 1358 cm.$^{-1}$ (in chloroform solution).

Bands practically identical with the intense tropolone frequencies at 1615, 1553, 1475, 1440, and 1255 cm.$^{-1}$ also occur in β-methyltropolone (V) and γ-thujaplicin (VI) (Scott and Tarbell, *loc. cit.*), and in a carbethoxytropolone which was recently sent to us for infra-red examination (Bartels-Keith and Johnson, *Chem. and Ind.*, 1950, 677). These bands, and particularly those at or near 1615, 1553, and 1255 cm.$^{-1}$, may therefore serve to characterize the
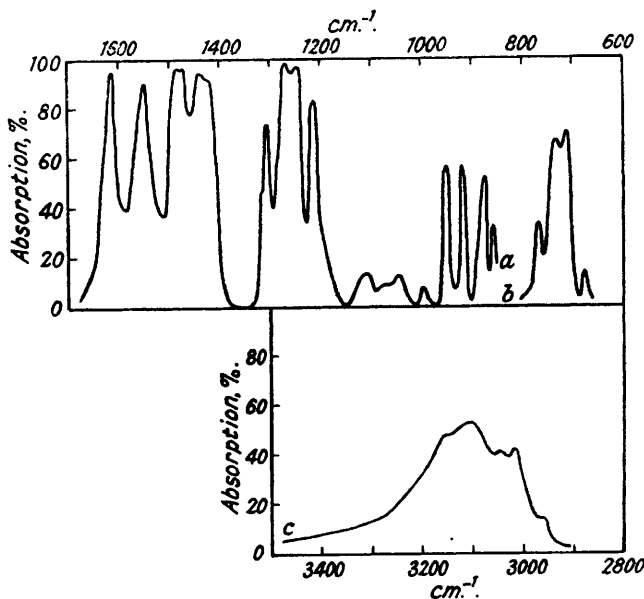
Infra-red spectrum of tropolone.

a, ~9% *in carbon tetrachloride,* 0·1 *mm. path length.*
b, ~3·5% *in carbon disulphide,* 0·1 *mm. path length.*
c, ~2% *in carbon tetrachloride,* 1 *mm. path length.*

presence of the tropolone nucleus in colchicine (Scott and Tarbell, *loc. cit.*) or other complex organic structures. On the other hand, the intense 720 cm.$^{-1}$ doublet of tropolone was not reproduced in the carbethoxy-derivative (Scott and Tarbell did not examine their spectra

(V.)

(VI.)

below 1200 cm.$^{-1}$), just as the analogous absorption region of ethylenic and aromatic derivatives is known to be highly sensitive to changes in nuclear substitution. We may therefore expect that, *e.g.*, α-, β-, and γ-substituted tropolones should be clearly differentiated in this spectral region.

Experimental.—The infra-red spectra of tropolone and its cupric and carbethoxy-derivatives were recorded by standard methods on a Grubb–Parsons single-beam automatic recording spectrometer, employing both sodium chloride and lithium fluoride prisms (cf. Barnard, Fabian, and Koch, *J.*, 1949, 2442). Crystalline specimens were examined as powders in paraffin or perfluorokerosene.