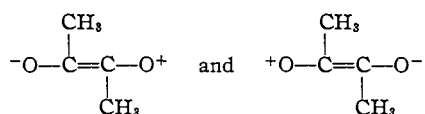


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Conjugation of Carbonyl Groups and the Absorption Spectrum of Triketopentane

BY MELVIN CALVIN AND C. L. WOOD

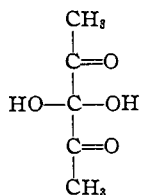
The nature of the interaction of a pair of adjacent or conjugated carbonyl groups as in diacetyl or quinone is not very clear and the interpretation of the electronic absorption spectra of this type of structure is especially uncertain by comparison with what may be done toward the interpretation of the color of conjugated systems involving only $C=C$, $C=N$, or $N=N$.¹ On the basis of the suggestions made by Lewis and Calvin,¹ one might expect the absorption of diacetyl to be due to the excitation of electronic oscillations represented by the extreme forms



This is made even more plausible by the fact that these forms already contribute considerably to the ground state of the molecule as is evidenced by the short distance (1.47 Å.) between carbonyl carbon atoms.²

The next member of the series, triketopentane, is not so readily interpreted. One cannot simply increase the length of the oscillators as is done for the extension of a conjugate carbon chain.

The only absorption datum which exists for triketopentane is the rather inconclusive measurement of Lifschitz³ taken on the chloroform solution. Since the triketone forms a very stable hydrate⁴ with water whose structure may be taken as



it is practically certain that solvation in chloroform toward structures of this type takes place with the consequent elimination of the central carbonyl group and the breaking of the conjugation between the two end ones. Consequently a number of samples of triketopentane were pre-

pared and their absorption spectra determined in pure paraffin hydrocarbon solvents.

Experimental

Preparation of the Triketopentane.—The triketone was made by two methods, that of Sachs and Barschall⁴ using nitrosodimethylaniline on acetylacetone, and by oxidation of acetylacetone with selenium dioxide.⁵

In a typical preparation by the method of Sachs and Barschall, 9 g. of nitrosodimethylaniline was dissolved in 30 cc. of alcohol in a flask and heated to boiling. Six grams of acetylacetone was added and the solution heated again to boiling. Then 1.1 cc. of sodium hydroxide (d. 1.36) was added all at once. The solution boiled strongly but not violently without further heating for about a minute. Slight heating caused the boiling to continue for another minute. At this point the solution was a clear dark red. Upon cooling in an acetone-solid carbon dioxide mixture, dark yellow crystals formed which were filtered out on a suction filter. The solution was cooled and filtered several times to recover all these crystals, which were the condensation product of acetylacetone and nitrosodimethylaniline, $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}=\text{C}(\text{COCH}_3)_2$.

These crystals were dissolved in 100 cc. of ether and 40 cc. of sulfuric acid (d. 1.16) added. This mixture was shaken in a separatory funnel and the ether solution poured off and saved. Then the sulfuric acid solution was heated to 60°, cooled and extracted three times with ether. The ether solutions were combined, the ether evaporated off, and the residue fractionated at 12 mm. The triketone came over from 52–54°. The yield was about 1 cc. or 16%. All the triketopentane prepared was immediately sealed in 8-cm. soft glass test-tubes until needed.

For the oxidation of acetylacetone by selenium dioxide, 17 g. of selenium dioxide was dissolved in 60 cc. of absolute alcohol and heated to boiling in a reflux apparatus. Then an equivalent quantity of acetylacetone was added in small amounts over a period of two hours, and the solution heated until the total time of heating was five hours and forty minutes. The solution became dark red and a precipitate formed. The liquid was decanted and distilled. Alcohol was distilled off at atmospheric pressure. The pressure was then reduced to 12 mm. and the liquid distilling at 53–55° was collected. About 1.5 cc. of an orange-red oily liquid with a strong but not unpleasant odor was secured. The 2,4-phenylhydrazone of triketopentane was produced from this liquid by the method of Sachs.⁴ The product of the second and third recrystallization melted at 156°, which was the melting point given by Sachs.

Triketopentane was produced by this method several times and a yield of 12% was the highest secured. However, it was found that the process could be expedited if the acetylacetone was added to the dry selenium dioxide, no solvent being used. Upon heating and shaking for five

(1) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939).

(2) LuValle and Schomaker, *This Journal*, **61**, 3521 (1939).

(3) Lifschitz, *Rec. trav. chim.*, **43**, 414 (1924).

(4) Sachs and Barschall, *Ber.*, **34**, 3047 (1901).

(5) Riley, Morley and Friend, *J. Chem. Soc.*, 1875 (1932).

minutes in an ordinary flask immersed in boiling water, a strong reaction takes place. The contents of the flask may be extracted with ether several times and the ether extract distilled. The residue left when the ether has distilled off contains triketopentane which will distil over at 53–55° at 12 mm. pressure. The yield is about the same as when a solvent is used.

The residue after the triketone is distilled off always contains a large amount of selenium, both combined and as the element. Upon heating strongly a foul smelling red oil may be distilled over. This upon standing will deposit red metallic selenium upon the walls of its container. This substance is probably a selenoketone. When less than an equivalent amount of selenium dioxide is used, the product is largely the addition compound of triketopentane and acetylacetone, $(\text{CH}_3\text{CO})_2\text{C}(\text{OH})\text{CH}(\text{COCH}_3)_2$.⁶

Absorption Spectra.—The absorption spectrum of triketopentane, prepared as described, was determined while dissolved in dry isoöctane. This isoöctane was 2,2,4-trimethylpentane, boiling at 99.3° and dried with metallic sodium. Extraordinary precautions had to be taken to keep the ketone dry, especially in the very dilute solutions required for absorption measurements. A tube was made with three side-arms grouped about a central tube having a diameter of about 20 mm. One side contained phosphorus pentoxide, another contained a mixture of isoöctane and phosphorus pentoxide. The third, which was very small, contained triketopentane contaminated with some water. The whole was sealed. This apparatus was allowed to stand for several days. Two or three times a day the triketone was heated to boiling in order to assist its dehydration by the phosphorus pentoxide. Care was taken that the triketone was not distilled into the central tube at this point. Finally about 0.1 cc. of the triketone was distilled into the central tube and then about 15 cc. of the dry isoöctane was distilled into the central tube also. The solution in the central tube was a clear orange-yellow. No crystals of hydrate were present and the solution did not change color upon standing for several weeks. If this solution was cooled strongly (below 0°), it became translucent; upon standing at this temperature it became clear, but lighter in color, and a drop of undissolved triketopentane formed in the bottom of the test-tube.

The spectrum of this saturated solution was obtained by means of a photographic prism spectrograph and also on a photoelectric grating spectrograph. The result is the same by both methods and is shown in Fig. 1 together with the spectrum of diacetyl in hexane solution taken on the same photographic instrument with the same dispersion. The spectrum of acetone in hexane solution also shown in Fig. 1 was taken from the work of Scheibe.⁷

Discussion

Two very clear and striking facts emerge from the comparison in Fig. 1: (1) there is very little shift toward the red of the first electronic band upon the insertion of the third adjacent carbonyl group, by comparison with the shift resulting from the change from one to two carbonyl groups; and

(6) Sachs and Wolff, *Ber.*, **36**, 3227 (1903).

(7) Scheibe and Frömel, Eucken-Wolf, "Hand- und Jahrbuch der chemischen Physik," **9**, III-IV, p. 144.

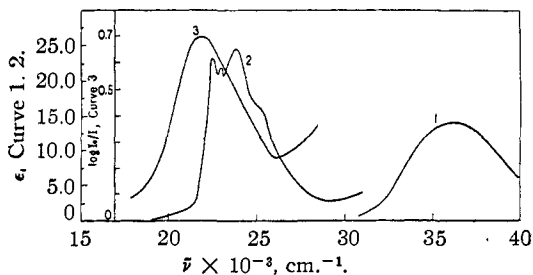


Fig. 1.—Curve 1, acetone in hexane at room temperature; Curve 2, diacetyl in hexane at room temperature; Curve 3, triketopentane in isoöctane at -50° , saturated solution in a 20-mm. cell.

(2) the vibrational structure so pronounced in diacetyl is totally lacking for triketopentane even at reduced temperatures. An examination of the spatial relationships in those molecules is necessary to an understanding of these effects.

The structure of diacetyl has been examined by means of electron diffraction⁸ and is described as predominantly the *trans* coplanar configuration shown in Fig. 2 with the dimensions $\text{CH}_3\text{—CO}$ 1.54 Å., CO—CO 1.47 Å., C=O 1.20 Å., $\text{H}_3\text{C—C=O}$ 123°, and O=C—CO 123°. In Fig. 2 and the following figures these interatomic distances and angles have been used and an attempt to represent the space actually occupied by each group or atom has been made by using spheres whose radii are about 85% of the values given by Pauling⁸ for the Van der Waals radii, namely, 1.4 Å. for oxygen and 2.0 Å. for the methyl group. The *cis*-coplanar configuration of

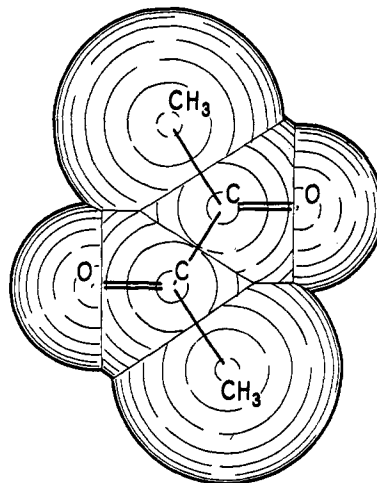


Fig. 2.—Diacetyl.

(8) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

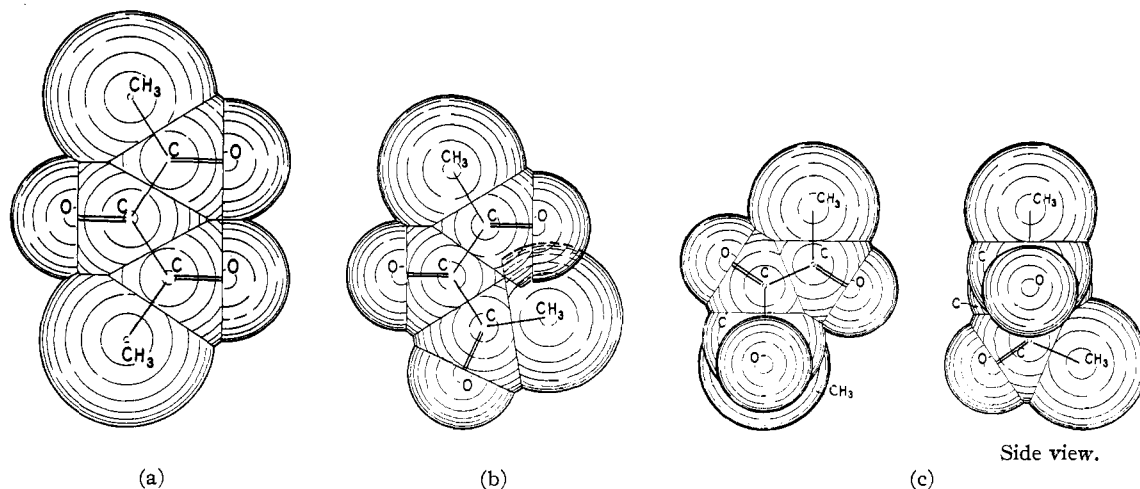


Fig. 3.—Triketopentane.

diacetyl is unstable for two reasons: (a) the interference of the methyl groups, and (b) the coulombic repulsions of the negative ends of the $C=O$ dipoles. The non-planar configuration of diacetyl is unstable with respect to the *trans*-coplanar one because (a) the coulombic energy of the *trans*-coplanar form is a minimum (the oxygens are at their greatest separation) and (b) the resonance forms of the type $\text{=O}-\text{C}=\text{C}-\text{O}\text{=}$ require

$$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ \text{O}-\text{C}=\text{C}-\text{O} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$$

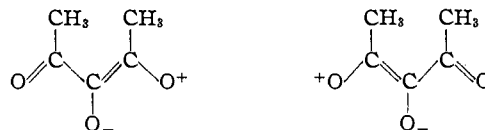
a totally coplanar configuration.

An exactly similar set of considerations apply to the case of the triketopentane whose dimensions cannot be very different from those of diacetyl. Of the three possible coplanar configurations the one shown in Fig. 3a is the most stable. Rotation of one CH_3CO group through 180° brings about the interference represented in Fig. 3b while rotation of both CH_3CO groups through 180° would produce an impossible structure in which both CH_3 groups are about in the same space. We have thus to consider only the coplanar structure of 3a and the non-coplanar structure of Fig. 3c, in which one of the CH_3CO groups has been rotated through an angle of 90° . In actual fact the maximum angle need not be, and probably is not, as great as 90° . There is still another non-coplanar form, that in which neither CH_3CO group is coplanar with the central carbonyl group, but this is indistinguishable from the last mentioned form at room temperature because of the thermal excitation of rotation or rather rotational oscillation of the CH_3CO groups.

A calculation of the difference in the coulombic energy between the coplanar configuration, Fig.

3a, and the 90° form of Fig. 3c, gives a practically negligible value being only about 500 cal. smaller in the non-coplanar form.⁹ The van der Waals repulsion between the oxygen atoms in the coplanar form should, however, be considerable since the oxygen-oxygen distance in Fig. 3a is only 2.4 Å. whereas twice the van der Waals radius of oxygen is 2.8 Å. On the other hand, any conjugation between the carbonyl groups will tend to keep the molecule coplanar. The essential point is that the twisting frequencies will be quite low.

The effect of these steric considerations upon the absorption spectrum of the triketopentane is quite easily deduced on the basis of the theory of Lewis and Calvin.¹ Since the molecule cannot attain the type of configuration necessary to permit the excitation of the linear oscillation represented by



the excited electronic state can involve an oscillation between only two of the $C=O$ groups at a time, and hence the absorption band cannot be shifted very far toward the red from that of diacetyl, as is indeed the case (see Fig. 1). Furthermore, the condition that the electronic excitation involves the establishment of a double bond along an axis about which there is a great tendency to excite thermal rotation permits an easy interchange of electronic energy and the thermal energy of the low frequency rotational oscillations

(9) This calculation is made using a $C=O$ distance of 1.20 Å. and a bond dipole of 2.7 debyes.

and hence the lack of any discernible vibrational structure in the band even at -50° .

Summary

1. The adsorption spectrum of triketopentane dissolved in an inert hydrocarbon solvent (isooctane) has been measured and compared with

that of diacetyl and acetone under similar conditions.

2. On the basis of this comparison of absorption spectra, together with a consideration of the molecular dimensions, non-coplanar structure is assigned to the triketopentane.

BERKELEY, CALIFORNIA RECEIVED SEPTEMBER 3, 1940

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Viscosity of Monolayers: a Test of the Canal Viscosimeter

BY GEORGE C. NUTTING AND WILLIAM D. HARKINS

Experimental and theoretical studies of the rate of flow of monolayers through surface slits or canals have been made by several investigators, among whom Bresler, Talmud and Talmud were the first.¹⁻⁶

For the limiting case of a deep and very narrow canal it has been proposed⁶ that the rate of flow is related to the absolute viscosity of the monolayer by the expression

$$\eta = \frac{(f_2 - f_1)a^3}{12(l)Q} - \frac{a\eta_0}{\pi} \quad (1)$$

in which f_2 and f_1 are the film pressures at the ends of the canal, in dynes per cm.; a is the width and l the length of the canal in cm.; Q is the area in sq. cm. of the film flowing through the canal in 1 sec.; and η_0 is the bulk viscosity of the subsolution at the temperature of the experiment. The first term is completely analogous to the Poiseuille formula for the flow of liquids through long capillary tubes. Applied to a film it presupposes that the canal width is small and that the ratio of length to width is large in order that flow may be laminar rather than turbulent and that end corrections may be negligible. It is also assumed that there is no slippage of the film along the sides of the canal.

The second term is a correction for the inevitable drag exerted upon a flowing film by the viscous fluid upon which it is spread. It has been derived for the case of a canal with smooth, parallel walls which extend below the surface to a distance much greater than the distance between the

walls. The conditions assumed in the development of this equation imply that the film is incompressible, and possesses a practically constant viscosity while passing through the canal. This obviously makes it necessary to keep the fall of film pressure in the canal as small as possible.

In the work presented in this paper the principal object was to determine what type of canal gives the best results, so large decrements of pressure have often been used. However, to minimize the effects of the change of area with pressure the investigations have been confined almost entirely to the alcohols, which give films of very low compressibility.

The Canal Viscosimeter and Experimental Methods

The procedure involved in the determination of viscosity is to measure the amount of film passing through the canal in unit time under a given pressure difference between the ends. The viscosimeter was assembled on a paraffined brass trough of inside dimensions $75 \times 25 \times 2$ cm. The film pressure on the entrance side of the canal was measured by means of a film balance, a detailed description of which has been given already.^{7,8} The film pressure was maintained constant by moving forward a barrier (piston) at a rate which just compensated for the loss of film from the high pressure side by its passage through the slit.

In much of the work the supports of the slit served as the barrier. That is, the slit itself was moved slowly forward as the experiment proceeded. The apparatus is diagrammed in Fig. 1b. The compressed film is contained in the area II between the float, A, of the film balance and the slit-barrier, B. III is a clean surface of 0.01 *N* sulfuric acid, and area I behind the slit contains the film material in so small an amount that the film pressure is negligible. The jaws of the slit were supported on brass rods 1.3 cm. square which rested on the sides of the trough. The forward and backward motion of the slit-barrier was accomplished through an accurately threaded rod (not

(1) Bresler, Talmud and Talmud, *Physik. Z. Sowjetunion*, **4**, 864 (1933).

(2) Dervichian and Joly, *Compt. rend.*, **204**, 1318 (1937).

(3) Joly, *J. Phys.*, **8**, 471 (1937); **9**, 345 (1938).

(4) Myers and Harkins, *Nature*, **140**, 465 (1937); *J. Chem. Phys.*, **5**, 601 (1937).

(5) Washburn and Wakeham, *THIS JOURNAL*, **60**, 1294 (1938).

(6) Harkins and Kirkwood, *J. Chem. Phys.*, **6**, 53, 298 (1938).

(7) Harkins and Myers, *ibid.*, **4**, 716 (1936).

(8) Nutting and Harkins, *THIS JOURNAL*, **61**, 1180 (1939).