[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Dipole Moments and Molecular Structures of Cycloheptatrienone and Three Tetracyclones[1,2]

BY ARMAND DI GIACOMO[3] AND CHARLES P. SMYTH

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The dielectric constants and densities of dilute solutions of four cyclic ketones in benzene have been measured and used to calculate the dipole moments of the molecules. The moment values are: cycloheptatrienone, 4.3; tetraphenylcyclopentadienone, 3.43; 2,5-bis-(4'-chlorophenyl)-3,4-diphenylcyclopentadienone, 4.6; tetrakis-(4-chlorophenyl)-cyclopentadienone, 2.26. The high moment of cycloheptatrienone confirms the indications of polarity given by other properties and gives evidence of resonance contributions from highly polar structures. Smaller contributions from more polar structures are indicated for tetraphenylcyclopentadienone. The moments of this molecule and of those of the two chlorine-substituted products are shown to be consistent with probable geometrical structures.

As the properties of the seven-membered ring ketone, cycloheptatrienone, suggested abnormally high polarity for the molecule, Prof. William E. Doering of Columbia University proposed to one of the writers the measurement of its dipole moment and very kindly provided a sample of the material. The results of this measurement are combined in the present paper with measurements on three ketones, possessing a five-membered ring with possibilities of contributions from resonating polar structures. Samples of these three substances were kindly furnished by Prof. Ernest I. Becker of the Polytechnic Institute of Brooklyn, who originally proposed the measurements. The writers are indebted to Professors Becker and Doering both for the materials and for advice as to their structures.

## Experimental Method

The measurements of dielectric constants and densities were carried out at 40° on dilute solutions in carefully purified benzene. The solutions of the tetraphenylcyclopentadienones or tetracyclones, which are deeply colored solids, difficultly soluble in benzene, were made up by adding hot benzene to a carefully weighed sample and stirring. When the solution cooled, it was weighed to the nearest milligram, the weight of benzene being obtained by difference. Cycloheptatrienone, a liquid, was transferred to the weighing bottle with the aid of a fine capillary syringe capable of delivering one gram of material in 100 drops. The solvent benzene was boiled before addition to prevent subsequent formation of air bubbles between the condenser plates and in the pycnometer.

The dielectric constants of the dilute solutions were measured with a heterodyne beat apparatus previously described.[4] A measuring cell of 10 cc. volume with gold cylinders of 110 $\mu\mu$f. capacitance was used. Density measurements were made with an Ostwald–Sprengel pycnometer in a manner similar to that previously described.[5] The molar polarization of the solute was calculated from the experimental data by the method of Halverstadt and Kumler.[6] The measured values of the dielectric constants, $\epsilon_{12}$, and specific volumes, $v_{12}$, of the solutions were found to be linear functions of the weight fractions, $w_2$, of the solutes according to the equations

$$\epsilon_{12} = \epsilon_1 + \alpha w_2$$

$$v_{12} = v_1 + \beta w_2$$

The values calculated for $\epsilon_1$, $v_1$, $\alpha$ and $\beta$ were used to obtain the polarization of the solute at infinite dilution

$$P_\infty = [3\alpha v_1/(\epsilon_1 + 2)^2 + (v_1 + \beta)(\epsilon_1 - 1)/(\epsilon_1 + 2)]M_2$$

in which $M_2$ is the molecular weight of the solute. The molar refractions for the D sodium line, $R_D$, were calculated from values of bond refractions in the literature[7] since they could not be measured directly because of the color of the compounds. Errors in the large moment values caused by this procedure were negligible. The dipole moment was then obtained from the usual equation

$$\mu = 0.01281 \times 10^{-18}[(P_\infty - R_D)T]^{1/2}$$

## Experimental Results

The values of the constants obtained in the calculation by the method of Halverstadt and Kumler are listed in Table I. The probable errors in the moment values are about ±0.1 $\times 10^{-18}$.

TABLE I

EMPIRICAL CONSTANTS AND POLARIZATIONS AT 40°

| $\epsilon_1$ | $v_1$ | $\alpha$ | $\beta$ | $P$ | $R_D$ | $\mu(10^{18})$ |
|---|---|---|---|---|---|---|
| Cycloheptatrienone | | | | | | |
| 2.2449 | 1.1659 | 17.532 | −0.2711 | 292.7 | 32.7 | 4.30 |
| Tetraphenylcyclopentadienone | | | | | | |
| 2.2444 | 1.1663 | 3.3894 | −0.3264 | 347.8 | 118.6 | 3.43 |
| 2,5-Bis-(4'-chlorophenyl)-3,4-diphenylcyclopentadienone | | | | | | |
| 2.2468 | 1.1665 | 4.9910 | −0.3957 | 541.6 | 128.3 | 4.61 |
| Tetrakis-(4-chlorophenyl)-cyclopentadienone | | | | | | |
| 2.2458 | 1.1663 | 1.2808 | −0.4611 | 237.9 | 138.1 | 2.26 |

## Discussion of Results

The considerable polarity indicated for the cycloheptatrienone molecule by its solubility in water, sparing solubility in ether, and high boiling point[8] is confirmed by its dipole moment 4.3 $\times 10^{-18}$ as compared to 2.76 for benzaldehyde, 2.89 for acetophenone and 2.97 for benzophenone in benzene solution.[9] These molecules show an increase of moment of only 0.1–0.2 $\times 10^{-18}$ over the aliphatic aldehydes and ketones, in which the moment is due primarily to resonance involving large contributions from polar structures such as $R_2C^+—O^-$. These slight increases in moment might be described in terms of additional small contributions from highly polar structures with positive charge on the ortho or para carbons of the ring. However, since the dimethylcyclohexanones

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[2] This paper represents a part of the work to be submitted by Mr. Armand Di Giacomo to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Proctor and Gamble Fellow in Chemistry, 1951–1952.

[4] L. M. Kushner and C. P. Smyth, THIS JOURNAL, **71**, 1401 (1949).

[5] G. L. Lewis and C. P. Smyth, *ibid.*, **61**, 3063 (1939).

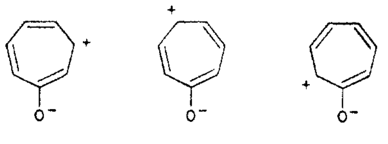
[6] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

[7] C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1931, Chap. VIII.

[8] W. E. Doering and F. L. Detert, THIS JOURNAL, **73**, 876 (1951).

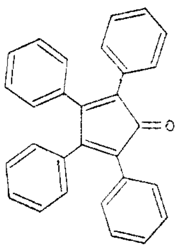
[9] L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948.

and other cyclic ketones have equally large moments,[9] it would seem that the small increases in moment are caused largely by electrostatic induction. For cycloheptatrienone, we may write six structures with a positive charge on the ring, such as

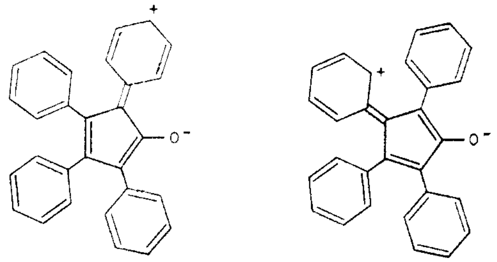


The large increase, about 1.4 × $10^{-18}$, in moment of this molecule over those of the other cyclic ketones seems to indicate the considerable stability of these polar structures with resonance increased by the possible existence of six, probably differing little from one another in energy.

The moment value 3.43 of 2,3,4,5-tetraphenylcyclopentadienone or tetracyclone, slightly lower than the value 3.61 reported by Bergmann and Fischer,[10] is less elevated than that of cycloheptatrienone, but still is about 0.5 × $10^{-18}$ larger than those of the previously cited cyclic ketones. In addition to the normal structure for the molecule,



and the polar structure characteristic of all ketones with the carbonyl carbon positive and the oxygen negative, twelve polar structures may be written, with a positive charge on one of the four para or eight ortho carbons of the four benzene rings, such as



As the moments of these structures are large, resonance involving very small contributions from each could cause the observed rise in moment. Evidently, the individual contributions of these twelve polar structures are much smaller than those of the six polar structures of cycloheptatrienone, since, although there are twice as many of them, and their moments are larger, the elevation of moment attributed to them is only 0.5 instead of 1.4. The stabilities of these structures must be greatly reduced by the steric repulsion between the phenyl groups, which prevents them from being coplanar with the five-membered ring.

The moments of di- and tetrachlorotetracyclone may be calculated on the basis of a model for the tetracyclone molecule. The moment due to each chlorine may be taken as that of chlorobenzene, 1.58 × $10^{-18}$, measured in benzene solution and its direction may be taken as that of the bond joining the five-membered ring to the chlorophenyl group. The tetracyclone moment acts in the direction of the axis of molecular symmetry, in which the carbonyl group lies. If, as a rough approximation, the five-membered ring is taken as a symmetrical pentagon with its five external valence bonds lying in the plane of the ring and their continuations bisecting the 108° angles at the pentagon corners, the moment of 2,5-bis-(4′-chlorophenyl)-3,4-diphenylcyclopentadienone should be

$$3.43 + 2 \times 1.58 \cos 72^\circ = 4.4$$

and that of tetrakis-(4-chlorophenyl)-cyclopentadienone should be

$$3.43 + 2 \times 1.58 \cos 72^\circ - 2 \times 1.58 \cos 36^\circ = 1.8$$

The dichlorotetracyclone moment thus calculated differs from the observed value by no more than the probable error, while the calculated value for the tetracyclone is a little low. The regular pentagon assumed in these calculations would be correct only if so much resonance occurred as to give all five bonds in the ring the same amount of double-bond character. Although the moment of tetracyclone is high enough to indicate that the contributions of the polar structures are sufficient to give a little double bond character to the three predominantly single bonds of the ring, the five bonds should certainly not be equivalent. If the five-membered ring is taken as having the structure indicated by electron diffraction[11] for cyclopentadiene with the C(CO)C angle 101° and the other ring angles 109° and 110°, and the external bonds of the ring are taken as making angles of 110° in the plane of the ring with the single bonds in the normal structure of the ring, the calculated moments are

$$3.43 + 2 \times 1.58 \cos 59.5^\circ = 5.04$$

$$3.43 + 2 \times 1.58 \cos 59.5^\circ - 2 \times 1.58 \cos 20^\circ = 2.07$$

Actually, the widening of these angles by the neglected fraction of double bond character in the three predominantly single bonds of the ring would lower the calculated values and give somewhat better agreement with the observed. Calculation shows that, if this external 110° angle on the 2- and 5-carbons is widened to 119°, a more probable value than 110°, the observed moment of the dichlorotetracyclone is exactly accounted for. To account exactly for the moment of tetrachlorotetracyclone it is then necessary to widen the other two 110° angles to 132°, rather too large an angle. However, it is evident that the moments of tetracyclone, and dichloro- and tetrachlorotetracyclone are consistent with a structure which receives small resonance contributions from highly polar structures and which, consequently, has a small amount of double bond character in the three single bonds of a planar five-membered ring and 120–130° valence angles for the external bonds of the ring.

A qualitative description of the charge distribu-

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(10) E. D. Bergmann and E. Fischer, *Mem. Soc. Chim.*, [5] **17**, 1084 (1950).

(11) V. Schomaker and L. Pauling, THIS JOURNAL, **61**, 1769 (1939).

tion in the cycloheptatrienone and cyclopentadienone rings is given by Brown's calculation[12] of the number of $\pi$-electrons per atom by the method of Coulson and Longuet-Higgins.[13] From the charge distribution and the dimensions of the tropolone ring given by X-ray analysis,[14] a dipole moment value $9.5 \times 10^{-18}$ may be calculated for cycloheptatrienone. A similar calculation gives $5.6 \times 10^{-18}$ for the hypothetical cyclopentadienone, irrespective of whether the ring is taken as a symmetrical pentagon or as resembling that of cyclopentadiene. The calculated moments greatly exceed the observed much as the values calculated for ionic structures tend to exceed such as may be observed,[15] but show that the molecular moments should be greater than those of ordinary aliphatic and aromatic ketones. The moment of the tetracyclone molecule is, presumably, increased above that of cyclopentadienone by the resonance contributions from the twelve polar structures with positive charge on a phenyl group. This would account for the fact that the tetracyclone moment is not as far below the value calculated for the cyclopentadienone ring as is the cycloheptatrienone moment below its calculated value.

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[12] R. D. Brown, *J. Chem. Soc.*, 2670 (1951).

[13] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947).

[14] J. M. Robertson, *J. Chem. Soc.*, 1222 (1951).

[15] *Cf.* C. P. Smyth, THIS JOURNAL, **63**, 57 (1941).

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

# Heat Capacity of Methane Adsorbed on Titanium Dioxide between 55 and 90°K.

BY E. L. PACE, D. J. SASMOR AND E. L. HERIC

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Some features in the construction and operation of a low-temperature adiabatic calorimeter for the study of gas–solid systems are described briefly. The heat capacity of methane adsorbed on titanium dioxide (rutile) has been determined between 55 and 90°K. at four coverages ranging from 0.2 to 1.0 monolayer. The heat capacity of the adsorbed methane is greater than that of solid methane and, at 89°K., exceeds the value for liquid methane. The heat capacity–temperature curves point to the absence of any first-order phase transitions in the range of temperatures and concentrations studied. It is suggested that the relatively high heat capacity of the adsorbed methane may be due in part to a contribution to the heat capacity resulting from a transition from localized to mobile adsorption. Additional experimental data and theoretical considerations are necessary before a complete model for the adsorption can be proposed.

Many investigations have been directed toward the determination of the state of the adsorbate and the nature of phase transitions in the adsorbate for systems of gases adsorbed on a finely divided solid. The isotherm measurements of the *n*-heptane–silver, *n*-heptane–ferric oxide, *n*-heptane–graphite systems[1-3] by Jura, Harkins and co-workers are particularly relevant to the present work. Analysis of the isotherms showed the presence of a first-order two-dimensional condensation in the adsorbed film. The two-dimensional critical temperature was found to be approximately 0.5 of the three-dimensional critical temperature, a value in rough agreement with theory utilizing a simple model[4] for the adsorbed gas. It was a purpose of the present investigation to observe directly and evaluate quantitatively a two-dimensional condensation by using a low-temperature adiabatic calorimeter in measurements of the heat capacity of the adsorbed film in the 50 to 90°K. temperature range. Such a transition would appear as a discontinuity in the heat capacity–temperature curve. The choice of methane as a suitable adsorbate was based on the following considerations. Its three-dimensional critical temperature of 190°K. made it reasonably probable that a two-dimensional condensation of the type observed by Jura and co-workers would occur in the temperature range to be studied. In addition, Hill[4] had pointed out that transitions from localized to mobile adsorption should occur at low temperatures. The spherical symmetry of the methane molecule was a desirable feature if any interpretation of the results in terms of structure was to be made. Titanium dioxide in the rutile form was selected as an adsorbent after a preliminary study of the adsorption isotherms indicated that it was satisfactory from the standpoint of surface area, non-porosity, and reversibility of adsorption.

The only comparable measurements are those of Simon and Swain[5] with the argon–charcoal system, Morrison and Szasz[6] with the nitrogen–rutile system, and Morrison, *et al.*,[7] with the argon–rutile system.

## Experimental

**Apparatus.**—The low temperature adiabatic calorimeter used in the experimental measurements followed essentially the same relative arrangement of cold reservoirs, radiation shields and calorimeter vessel as employed by Yost, *et al.*,[8] in calorimetric studies of condensable gas systems. Because the activation of the adsorbent required the use of elevated temperatures with the calorimeter vessel containing the solid adsorbent, the construction of the calorimeter and the arrangement of the electrical leads, difference thermocouples, etc., was accomplished in such a manner as to allow convenient disassembly of the apparatus. Morrison and Los[9] have utilized a calorimeter of similar design in a study of the argon–rutile system.

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[1] G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *J. Chem. Phys.*, **13**, 535 (1945).

[2] G. Jura, E. H. Loeser, P. R. Basford and W. D. Harkins, *ibid.*, **14**, 117 (1946).

[3] G. Jura, W. D. Harkins and E. H. Loeser, *ibid.*, **14**, 344 (1946).

[4] T. L. Hill, *ibid.*, **14**, 441 (1946).

[5] F. Simon and R. C. Swain, *Z. physik. Chem.*, **B28**, 189 (1935).

[6] J. A. Morrison and G. J. Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

[7] J. A. Morrison, J. M. Los and L. E. Drain, *Trans. Faraday Soc.*, **47**, 1023 (1951).

[8] D. M. Yost, C. S. Garner, D. W. Osborne, T. R. Rubin and H. Russell, Jr., THIS JOURNAL, **63**, 3488 (1941).

[9] J. A. Morrison and J. M. Los, *Discussions Faraday Soc.*, No. 8, 321 (1950).