aliphatic series through B-strain[45] and steric inhibition to solvation of the oxonium ion. Thus, there seems to be little doubt that alcohols are considerably more basic than their cognate ethers[45,46] in contrast to the simple secondary amines which are usually more basic than primary amines of the same carbon content.[4] The large increase in basicity that accompanies branching close to the ether oxygen in the phenolic ethers we have studied, shows that these base-weakening factors are overwhelmed by strengthening factors and in view of the usually modest contributions from the inductive effects of alkyl groups and the large effects that we have seen from steric inhibition of resonance, we believe that the latter is the main factor when branching is close to oxygen. Further evidence that inductive effects are inadequate to explain these increases is obtained by plotting Taft's[47] σ^*-values for the alkyl groups *vs.* the pK_a's of the alkyl phenyl ethers. Only a wide scatter of pointsis seen.

Acknowledgment.—We are grateful to the National Science Foundation for help in the purchase of the infrared spectrophotometer and to the National Institutes of Health for the purchase of the Cary 14.

[46] R. L. Burwell, Jr., and M. E. Fuller, THIS JOURNAL, **79**, 2332 (1957).

[47] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 591.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NAGOYA UNIVERSITY, CHIKUSA, NAGOYA, JAPAN]

The Dipole Moments of Some Heptafulvene Derivatives

BY MASUMI YAMAKAWA, HARUYUKI WATANABE, TOSHIO MUKAI, TETSUO NOZOE AND MASAJI KUBO

RECEIVED MAY 23, 1960

The dielectric constants and densities of dilute solutions of heptafulvene-8,8-dinitrile, 8-ethoxycarbonylheptafulvene-8-nitrile, tropylmalononitrile, ethyl tropylcyanoacetate, diethyl tropylmalonate, ditropylmalononitrile and ethyl ditropylcyanoacetate in benzene or dioxane have been measured and used to calculate the dipole moments of the molecules. From these data, the moments of heptafulvene and 7-methylcycloheptatriene were calculated to be 3.07 and 0.13 D. In the former compound, the negative end of the moment is on the side of a methylene group, while in the molecule of the latter compound negative charges accumulate in the ring at the expense ot those around the carbon atom of a methyl group.

Introduction

Measurements have already been made on the dipole moments of tropone, tropolone and a number of their derivatives,[1] and the results have been used for the elucidation of the structures of these molecules. One of the simplest and the most fundamental molecules having a cycloheptatriene ring is that of heptafulvene, which, however, is not stable and readily polymerizes.[2] The molecule of this compound is feasible for theoretical treatment. In fact, Berthier and Pullman[3a] discussed this problem by both the valence bond method and the molecular orbital method, the moment calculated by the latter method being 2.35 D.; later, Bergmann, *et al.*,[3b] carried out a molecular orbital treatment on this molecule and gave a moment of 4.6 D. in rather poor agreement with the value mentioned above. However, these authors seem to lay emphasis on the direction of the moment in the molecule rather than on the exact numerical magnitude. They predicted that the molecule of heptafulvene has a moment with its negative pole at a methylene group, whereas the moment of a fulvene molecule is directed along the opposite direction. Against these authors' prediction, a contradictory opinion was raised by Julg,[4] who applied a seld-consistent molecular field method to a heptafulvene molecule. The results of his calculation differ considerably from those obtained by the aforementioned LCAO method, the dipole moment being calculated as 0.14 D. in the opposite direction to that given in the older references.

The present investigation was undertaken in order to determine both the magnitude and the direction of the moment of heptafulvene on the basis of the observed moments of some heptafulvene derivatives. The dipole moments of some compounds having a tropyl group or groups were also studied for comparison.

Experimental Method and Results

The samples of heptafulvene-8,8-dinitrile (I, m.p. 200°), 8-ethoxycarbonylheptafulvene-8-nitrile (II, m.p. 63.5°), tropylmalononitrile (III, m.p. 63°), ethyl tropylcyanoacetate (IV, b.p. 138–141.5° (5 mm.)), diethyl tropylmalonate (V, b.p. 128–132° (4 mm.)), ditropylmalononitrile (VI, m.p. 107°) and ethyl ditropylcyanoacetate (VII, m.p. 125°) were synthesized and purified by two of the present authors (T. M. and T. N.) in Tohoku University.[5] The measurements of dipole moments were carried out at 25° on dilute solutions in benzene, except heptafulvene-8,8-dinitrile, which was sparingly soluble in this solvent and therefore was studied in dioxane solutions. The dielectric constants were measured by means of a heterodyne beat apparatus provided with a platinum cell.[6] For each solute, determinations were made on solutions of four different concentrations appropriately chosen below 3 weight per cent. The graphical plot of the dielectric constant as well as the density of solutions against the concentration in weight per cent. gave linear dependence within experimental errors. The slopes of these straight lines were evaluated by the least-squares method and the

[1] M. Kubo, *et al.*, *Bull. Chem. Soc. Japan*, **24**, 10, 99 (1951); **26**, 192, 242, 272 (1953); **27**, 364 (1954); P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).

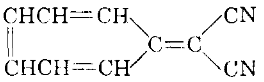
[2] W. von E. Doering, "Theoretical Organic Chemistry," Butterworths Scientific Publications, London, 1959, p. 35.

[3] (a) G. Berthier and B. Pullman, *Trans. Faraday Soc.*, **45**, 484 (1949); (b) E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. soc. chim. France*, 684 (1951).

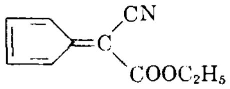
[4] A. Julg, *J. chim. phys.*, **52**, 50 (1955).

[5] T. Nozoe, T. Mukai, A. Sato and I. Osaka, *Bull. Chem. Soc. Japan*, to be published.

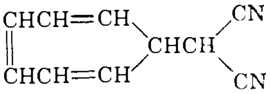
[6] Y. Kurita and M. Kubo, THIS JOURNAL, **79**, 5460 (1957). B. Eda, K. Tsuda and M. Kubo, *ibid.*, **80**, 2426 (1958).



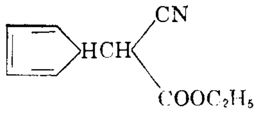
Heptafulvene-8,8-dinitrile (I)



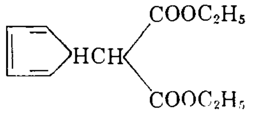
8-Ethoxycarbonyl heptafulvene-8-nitrile (II)



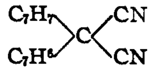
Tropylmalononitrile (III)



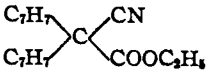
Ethyl tropylcyanoacetate (IV)



Diethyl tropylmalonate (V)



Ditropylmalononitrile (VI)



Ethyl ditropylcyanoacetate (VII)

molar polarization of the solute was calculated by a method similar to that introduced by Halverstadt and Kumler,[7] differing in that densities were used rather than the specific volumes. The deformation polarization of each compound was assumed to be 1.05 times the molar refraction approximated with the sum of atomic refractions for the D line. Since the values of moments are great, no serious errors are introduced by this assumption, probable errors being estimated at less than 0.05 D.

The results are shown in Table I, in which ϵ_1 and d_1 denote, respectively, the dielectric constant and density of the solvent; α and β are, respectively, the changes of the dielectric constant and density of solutions with the weight fraction of the solute; other notations have their usual significances.

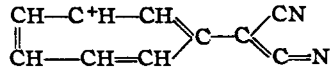
TABLE I

DIPOLE MOMENTS OF SOME DERIVATIVES OF HEPTAFULVENE OR 7-METHYLCYCLOHEPTATRIENE IN BENZENE (ϵ_1 = 2.273, d_1 = 0.8728, II–VII) OR DIOXANE (ϵ_1 = 2.210, d_1 = 1.0283, I) SOLUTIONS AT 25°

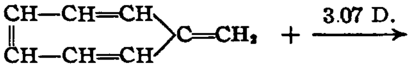
Compd.	α	β g./cc.	$P_{2\infty}$ cc.	MR_D cc.	μ D.
I	45.48	0.0908	1194	44.2	7.49
II	10.67	.219	455.7	55.4	4.40
III	11.93	.171	393.6	44.6	4.12
IV	6.844	.168	316.1	54.2	3.56
V	2.646	.178	192.7	67.1	2.44
VI	8.547	.173	464.5	73.7	4.35
VII	4.438	.205	319.7	84.9	3.35

Discussion of Results

The molecule of heptafulvene-8,8-dinitrile involving no axis of internal rotation is particularly suitable for the estimation of the moment of heptafulvene. Let it be assumed for bond moments that μ(H—C) = 0.4 D. and μ(C≡N) = 3.5 D.[8] The valency angle ∠C–C–C of a carbon atom =C< is reported to be 111.5° in tetramethylethylene and isobutylene[9] as determined by electron diffraction. However, considering the conjugation between the ring and CN groups, the value, 117°, calculated by Whiffen[10] from the microwave data of acrylonitrile[11] is presumed to be a closer approximation to the corresponding angle in the molecule under investigation. Then, from the observed moment of heptafulvene-8,8-dinitrile, 7.49 D., the moment of heptafulvene is estimated at 3.42 D. However, this value must represent surely an overestimation, because in the molecule of the former compound conjugation exists between π-electrons in a cycloheptatrienylidene group and those in CN groups, whereas such is not the case with heptafulvene. In other words, resonance among various electronic structures of the type



will contribute to an increase in the moment of heptafulvene-8,8-dinitrile. The extent of the overestimation is open to speculation, but a rough estimate thereof is afforded by a comparison between the moment (3.90 D.) of benzonitrile[12] and that (3.50–3.60 D.) of alkyl cyanides having nearly the same number of carbon atoms. Accordingly, one may presume that the moment of heptafulvene is not far from 3.07 D.



The moment 2.35 D. calculated by Berthier and Pullman[3a] is smaller while the value 4.6 D. obtained by Bergmann, *et al.*,[3b] is greater than the value of the present investigation. It is noteworthy that the direction of the moment concluded on the basis of experiments is in agreement with predictions by these authors. Berthier and Pullman[3a] and Bergmann, *et al.*,[3b] obtained values for the moment differing from each other to a considerable extent, in spite of using practically the same semi-empirical molecular orbital method. The reason for this seems to lie in an assumption made by the former authors that the resonance integral between two adjacent carbon atoms bonded by a single bond in the ordinary structural formula is 0.8 times as great as that between carbon atoms bonded by a double bond in the same formula, whereas the latter authors attributed the same exchange integral to all CC bonds. In view of the fact that electron diffraction investigation on tropolone[13] and tropone[14] as well as X-ray crystal analysis on tropolone derivatives[15] indicated the presence of a carbon ring having an essentially regular heptagon form, the calculation by Bergmann, *et al.*, is presumed to be more reasonable.[16] However, since the

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(7) I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

(8) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 244.

(9) L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).

(10) H. J. M. Bowen, *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

(11) W. S. Wilcox, J. H. Goldstein and J. W. Simmons, *J. Chem. Phys.*, **22**, 516 (1954).

(12) This and the following values are moments in benzene at room temperature: L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, MIT, Mass., 1948.

(13) M. Kimura and M. Kubo, *Bull. Chem. Soc. Japan*, **26**, 250 (1953).

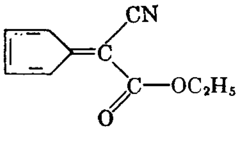
(14) K. Kimura, S. Suzuki, M. Kimura and M. Kubo, *J. Chem. Phys.*, **27**, 320 (1957); *Bull. Chem. Soc. Japan*, **31**, 1051 (1958).

(15) Y. Sasada, K. Osaki and I. Nitta, *Acta Cryst.*, **7**, 113 (1954); Y. Sasada and I. Nitta, *ibid.*, **9**, 205 (1956).

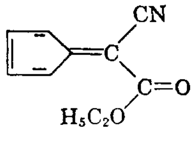
(16) B. Pullman and A. Pullman, "Les Théories Électroniques de la Chimie Organique," Masson & Cie, Paris, 1952.

molecular orbital method underestimates, in general, repulsions between electrons, it is plausible that they obtained a moment slightly greater than that of the present investigation. On the other hand, the moment predicted by Julg[4] does not agree with the present experiment in regard to both the direction and the magnitude of the moment. The moment of heptafulvene represents perhaps the greatest one ever reported for a hydrocarbon molecule, but the value is adequate compared with the large moment, 4.17 D., of tropone.[17] Presumably, the lack of stability of heptafulvene is closely associated with the high polarity of the molecule.

The moment of 8-ethoxycarbonylheptafulvene-8-nitrile is hardly feasible for a rigorous theoretical treatment. However, the observed moment is consistent with the structure I, whereas an alternative planar form II gives a too high theoretical moment (>7 D.) incompatible with the observed moment. This is quite understandable, because the molecule will be stabilized with its CN and C=O groups of high polarity separated farthest apart from each other.

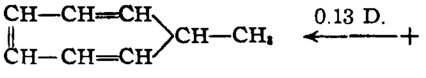


I



II

The molecule of ditropylmalononitrile is suitable for the estimation of the moment of 7-methylcycloheptatriene, the simplest molecule having a tropyl group. The moment calculated for this compound is 0.13 D. Although the use of the moment of a tropyl group is open to question, because there is no assurance that the group moment is parallel to the end C—C axis, it leads to a calculated moment, 4.43 D., for tropylmalononitrile in fair agreement with the observed value of 4.12 D. The problem of various valence structures for compounds having a tropyl group has been a subject of considerable dispute among organic chemists[18] and the nuclear magnetic resonance has been employed in order to discuss the structure of some of these compounds. However, the present discussion is independent of choice to be made among conceivable valence structures for a tropyl group.



$$\begin{array}{l} CH{-}CH{=}CH \\ \| \qquad\qquad\qquad \rangle CH{-}CH_3 \\ CH{-}CH{=}CH \end{array} \qquad \xleftarrow{0.13\ D.}+$$

Mention should be made that the estimated moment for heptafulvene, 3.07 D., is much greater than that for 7-methylcycloheptatriene, 0.13 D., and that the directions of the moments are opposed. The former compound is a typical example of non-alternant hydrocarbons which show a π-electron moment. On the other hand, although the molecule of the latter compound contains an odd-member ring, it has a character of an alternant hydrocarbon as a π-electron system, because one of the carbon atoms in the ring is bonded to four other atoms, the bond type being that of sp^3 rather than of sp^2. Since π-electrons in alternant hydrocarbons are predicted[19] to be uniformly distributed over carbon atoms involved, the π-electron moment vanishes. Thus, the difference in polarity between heptafulvene and 7-methylcycloheptatriene can be explained qualitatively in terms of the theory of molecular orbitals.

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[17] Y. Kurita, S. Seto, T. Nozoe and M. Kubo, *Bull. Chem. Soc. Japan*, **26**, 272 (1953).

[18] W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, This Journal, **78**, 5448 (1956).

[19] C. A. Coulson, H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A192**, 16 (1947); C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

[Contribution from the Detroit Research Laboratories of the Ethyl Corp., Detroit, Mich.]

The Chemistry of Cyclopentadienylmanganese Tricarbonyl Compounds. II. Sulfonation and Metallated Derivatives[1]

By Michael Cais[2] and John Kozikowski

Received March 14, 1960

Cyclopentadienylmanganese tricarbonyl has been sulfonated. A number of sulfones prepared from the sulfinic acid and sulfonyl chloride are reported. The sulfinic acid also served as starting material for the preparation of ring mercurated derivatives of cyclopentadienylmanganese tricarbonyl.

Recently, Piper, Cotton and Wilkinson[3] have carried out a study of the structure of cyclopentadienyl–carbon monoxide compounds of transition metals. These authors point out that the case of cyclopentadienylmanganese tricarbonyl (I) is a very interesting one because the cyclopentadienyl ring is considered to be bound to the metal by a "sandwich" bond, whereas in manganese bis-cyclopentadienide (II) the metal to ring bond appears to be of ionic character.[4,5] A striking difference between the two compounds is that I does not react with maleic anhydride whereas II reacts instantaneously with the latter.[5] This and other differences between compounds I and II, in particular the suggested presence of a "sandwich" bond in I, made it seem desirable to us to investigate the chemical properties of I. This investigation was directed

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[1] Presented in part at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 14–18, 1959.

[2] Chemistry Department, Technion, Haifa, Israel.

[3] T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. and Nuclear Chem.*, **1**, 165 (1955).

[4] G. Wilkinson and J. M. Birmingham, This Journal, **76**, 6210 (1954).

[5] G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. and Nuclear Chem.*, **2**, 95 (1956).